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THE MEASUREMENT OF HYDROGEN ION CONCENTRATION

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THE MEASUREMENT OF HYDROGEN ION CONCENTRATION

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WITH ILLUSTRATIONS AND DIAGRAMS

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PREFACE

LESS than a decade ago the conception of hydrogen ion concentration as a more exact expression of acidity, or rather of reaction, than titratable acidity or alkalinity was mainly of academic interest. Soon, however, it began to be realised that the extension of this conception to technological science provided not only a solution to a number of problems but also in certain processes, a valuable means of control. The study of the subject then spread into so many of the ramifications of industry that it became almost a chemical craze, and evoked bitter though not altogether unjustifiable criticism from the older schools of chemists, who realised perhaps the limitations of the theories on which it was based.

The first wave of enthusiasm for what has been styled "hydrogen *Ikon* worship" has now subsided, and discerning workers have realised that hydrogen ion concentration, if not a panacea as was once thought, at all events serves as a cure for many ills if applied with judgment and considered in conjunction with other factors. The list of industries dealt with in Part IV, though incomplete, is an indication of the widespread application of the subject.

Hitherto the worker in the industrial laboratory who has little or no knowledge of electrochemistry but who feels that a study of hydrogen ion concentration is essential for his purpose, has been in an unfortunate position. He can, of course, consult the exhaustive standard works on the subject. Such works, however, though mines of information to the academic worker, are of much less value to the works' chemist whose main study is often entirely different in character, and who has little opportunity to master the whole of the theoretical basis of hydrogen ion concentration measurements. The only alternative is the periodical literature, but in both cases he is faced with the difficult task of finding out exactly what is most useful to him out of a tremendous amount of strange information. In addition, it should be pointed out that in this of all subjects a little knowledge is dangerous, and may lead, quite unconsciously to the worker, to false results.

The writer has therefore thought for some time that there is a real need for a small book which gives the shortest and simplest account of the theoretical side of the subject consistent with the needs of the worker, together with a straightforward description of the methods used, in which no previous knowledge of electrochemistry is assumed. This opinion has been confirmed by colleagues in industry, and the present volume is an attempt to fill the gap.

The needs of the busy worker on strange ground have been borne in mind throughout. Thus, where possible, the apparatus has been chosen so that measurements may be carried out in laboratories not normally equipped for physico-chemical experiments, while the methods described are those which have been found to give the most reliable results. In addition, numerous pitfalls and sources of error are indicated, and a novel feature is Part IV, which is devoted to special modified methods of use in particular cases or in connection with certain industries. Rapid methods of calculation are described, and the tables of data collected at the end of the book have been compiled from the most recent and reliable information. A large number of selected references to the literature has also been included (at the end of each Part) for those who wish to study the subject further, and it is hoped that the book may thereby prove useful not only to the student and works' chemist, but also to the research worker.

In common with all who study this subject the author desires to express his acknowledgments to W. Mansfield Clark's classic work, *The Determination of Hydrogen Ions*. His thanks are also due to the firms who have kindly permitted him to reproduce illustrations of their apparatus, and particularly to his wife for her invaluable assistance in the preparation of the manuscript.

J. G.

London,
March, 1930.

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THE MEASUREMENT OF HYDROGEN ION CONCENTRATION

PART I

INTRODUCTION

CHAPTER I

THEORY

THE description of substances as "acid" and "alkaline" dates from the beginnings of chemical science. Even to-day the term "acidic" is used to indicate sourness, while substances which feel soapy when dissolved in water are often termed "alkaline." The textbooks of the last generation describe acids and alkalies in terms of their opposite effects on the colour of litmus paper, and the two words have thus in a sense become antonyms. This tendency to regard acids and alkalies as opposites was, no doubt, based on the fact that the distinctive properties of the one could be neutralised by addition of the other. Indeed, the "killing" effect of an alkali on an acid was to the early chemists the principal means by which it could be recognised. It will be shown later that these properties of acids and alkalies are of significance only from the descriptive point of view, and that acidity and alkalinity are not opposites, but merely represent stages or levels on a common scale.

THE THEORY OF ELECTROLYTIC DISSOCIATION (IONISATION) *

It was Arrhenius [1] in 1887 who laid the foundations on which is built the theory of hydrogen ion concentration and all that it implies. The dissociation theory of electrolysis which his work placed on a sound experimental basis, is so fundamental that a

* A distinction should be noted between *dissociation*, the splitting up of molecules into atoms or groups of atoms, and *ionisation*, which is dissociation into ions.

[1] Such numbers refer to the list of references given at the end of each Part.

brief description of it in its simplest form is essential in order to explain what follows.

Ionisation and Electrolysis.—It is well known that according to the theory, substances such as acids, alkalies, and salts (known as *electrolytes*), whose aqueous solutions conduct electricity, may be considered to be split up in solution into two portions or *ions*. One (the *cation*) carries a positive charge, and will therefore be attracted to a negatively charged plate or electrode (*cathode*) placed in the solution; the other (the *anion*) is negatively charged and travels through the solution to the *anode* or positively charged electrode. At the respective electrodes the charges on the ions are neutralised, and the ions then become uncharged atoms and immediately assume the properties of such atoms as they are commonly known. This decomposition of electrolytes into their constituents is known as *electrolysis*, and the mechanism controlling it was first suggested by Faraday in 1834. Incidentally, there is no rigid distinction between electrolytes and non-electrolytes, but rather a gradual transition from substances which are strongly ionised to those which are not ionised at all.

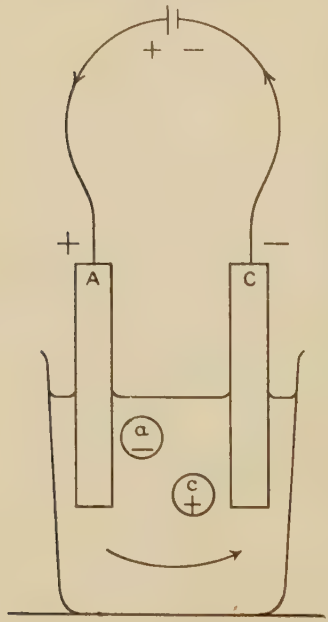

FIG. 1.

It should be noted further that although electrolytes are split up into ions (ionised) as soon as they are dissolved, electrolysis, or the passage of ions through the solution and the neutralisation of their charges at the electrodes, does not proceed spontaneously, but requires some external energy. This may be supplied by means of an electric cell such as an accumulator, the positive or negative terminals of which are connected to what are to be the positive and negative electrodes of the electrolytic cell respectively. The ions will then move to their respective electrodes, or in other words, a current will flow through the solution in the manner pictured in Fig. 1 in which the arrows represent the direction of the positive current, and *a* and *c* represent an anion and cation respectively. The conduction of electricity by electrolytes differs essentially from conduction by metals inasmuch

as it depends on the rate at which the ions are discharged, on their number, and on their rate of travel through the solution.

Faraday's Laws.—Now, according to Faraday's laws, (1) the amount of any substance deposited is proportional to the quantity of electricity flowing through the electrolyte, and (2) the amounts of different substances deposited by the same quantity of electricity are proportional to their equivalent weights. The unit of *quantity of electricity* is the amount conveyed in 1 second by a current of 1 ampere, and is known as the *coulomb*. Highly accurate experiments have been made on the deposition of silver by electrolysis, and it has been found that 0·00111800 grm. is deposited by 1 coulomb. From this the amount of any other element deposited by 1 coulomb may be calculated from the ratio of the equivalent weights (*i.e.*, atomic weight/valency) of silver and of the element concerned.

Since 0·001118 grm. of silver is deposited by 1 coulomb, 1 grm.-equivalent of silver (*i.e.*, the atomic weight expressed in grms.) is deposited by $\frac{107{\cdot}88}{0{\cdot}001118}$=96,493·7 coulombs, the atomic weight of silver being taken as 107·88. The above two laws may now be summarised in the statement that 96,493·7 coulombs are required to deposit 1 grm.-equivalent of any element. The quantity 96,493·7 coulombs is called the *faraday* * (*F*), though the value actually accepted by international agreement is 96,500 coulombs.

Having defined the faraday by the equation

$$F=96{,}500 \text{ coulombs},$$

let us return to

The Dissociation of Electrolytes.—What are the two portions or ions into which an electrolyte is split in solution? We know that a salt,† a typical electrolyte, is always formed by the union of an acid and a base with the elimination of water. Thus, in the case of the formation of sodium chloride from hydrochloric acid and sodium hydroxide we have

$$HCl+NaOH=NaCl+H_2O.$$

The water is always derived from the atoms constituting the acid and alkali.

* Not to be confused with the *farad*, the unit of electrostatic capacity. See the *International Critical Tables* for the derivation of these and other accepted definitions.

† The term *salt* (Latin *sal*) was formerly applied to the substance now known commonly by that name. Its use then spread gradually to all substances which could be crystallised from water, until a realisation of the relationship between acids, bases, and the products of their neutralisation led to the present definition.

Now, in general, a salt may also be formed from an acid by the action of a metal, *e.g.*,

$$H_2SO_4+Zn=ZnSO_4+H_2,$$

but in this case hydrogen only is produced, and not water.

On these grounds alone, therefore, there is a good deal of justification for representing an acid in its general form as a combination of hydrogen H and another portion A—viz. as HA. A base, which provides the remainder of the water molecule, will then be represented BOH, so that the formation of the salt AB is represented by

$$HA+BOH=AB+H_2O.$$

On the basis of the ionic theory this equation becomes

$$(H^{\cdot}+A')+(B^{\cdot}+OH')\rightarrow(A'+B^{\cdot})+(H^{\cdot}+OH').$$

According to the customary notation a dot and a dash represent a single positive charge and negative charge on an ion respectively. Thus two or more dots and dashes would represent two or more such charges, while the same numbers of dots and dashes occurring together in the same molecule or group of atoms represent electrical neutrality, *e.g.*, $(A'+B^{\cdot})$.

We have thus arrived at the nature of the pairs of constituents into which electrolytes dissociate in solution. Thus,

$$\begin{array}{ll}\text{Acids—} & HA\rightarrow H^{\cdot}+A'\\ \text{Bases—} & BOH\rightarrow B^{\cdot}+OH'\\ \text{Salts—} & AB\rightarrow B^{\cdot}+A'.\end{array}$$

It remains now only to show why the ions $B^{\cdot}$ and $H^{\cdot}$ should be given positive charges, while A' and OH' bear negative charges. As a matter of fact this follows at once from the simple application of Faraday's laws to the electrolysis of water. When water is electrolysed in the manner already indicated, it is split up into hydrogen which appears at the cathode, and oxygen which appears at the anode, and the amounts obtained per faraday may be calculated from the respective equivalent weights. It will at once be asked why oxygen and not " OH " is produced at the anode, and the answer expressed in ionic form is:

$$2H_2O\rightarrow 2(H^{\cdot}+OH')\rightarrow 2H^{\cdot}+2OH'\rightarrow H_2+2OH'.$$

The H_2 is liberated at the cathode as a molecule of hydrogen, whilst the two OH' ions are left at the anode. As they cannot exist in molecular form they undergo transformation into an oxygen atom, which is evolved as gas, and water:

$$2OH'\rightarrow H_2O+O.$$

This water molecule is then decomposed again in the same way, in conjunction with a similar molecule, so that the combined effect is represented in terms of atoms and molecules as

$$2H_2O = 2H_2 + O_2.$$

The quantities of hydrogen and oxygen obtained, as represented by this equation, are obviously in agreement with Faraday's law.

Not only does the theory show us the nature of the charges on the ions of an electrolyte, but it also explains the colours and reactions of solutions of salts in terms of those of the constituent ions, and provides us with definitions of acids and bases as follows:

An acid is a substance which in solution is dissociated into positively charged hydrogen ions ($H^{\cdot}$) and a negatively charged residue; a base is dissociated in solution into negatively charged hydroxyl (OH') ions and a positively charged residue. It is difficult to distinguish between an alkali and a base. The former term is used in a general sense for soluble hydroxides of metals or of ammonia, whilst a base is essentially a salt-forming substance which yields OH' ions in solution.

These statements are to replace the descriptive definitions of the early workers, and are the basis of the subject with which this book deals. Their importance, moreover, is such as to warrant the foregoing statement of the very elementary principles from which they are derived.

Strong and Weak Acids and Bases

We know that if we prepare decinormal solutions of, say, hydrochloric acid and acetic acid, these solutions are of the same strength in the sense that the same volume of each will be neutralised by exactly the same volume of a decinormal solution of alkali such as sodium hydroxide. But if we taste these acid solutions we are aware of a very great difference. In brief, the acid properties (*e.g.*, sourness) or avidity of the hydrochloric acid is far more pronounced than that of the acetic acid. If we made up decinormal solutions of a number of acids and bases we should find that they could be roughly graded according to properties such as acid taste or soapy feel, etc. Actually there are more exact methods of grading acids and bases in this way (*e.g.*, from the heat produced on neutralisation and the readiness with which one acid displaces a base or another acid from a salt), but they all give approximately the same results, and it is convenient to refer only to those properties which require no explanation.

It seems, therefore, that the term " strength " may have two meanings—one to express what we prefer to call concentration or normality, and the other to express the acid or alkaline properties of a solution.

Degree of Ionisation.—Since we have agreed that $H^{\cdot}$ and OH' ions are responsible for the characteristic properties of acids and bases respectively, it is natural to suppose that a solution of a strong acid (strong in the second sense mentioned above) will contain more $H^{\cdot}$ ions than a solution of a weak acid of the same "concentration." But since, from our definition of concentration as normality, the number of hydrogen atoms available for ionisation in each case is the same, it follows that differences in the number of hydrogen ions actually present are accounted for by differences in the extent of the ionisation. Similar arguments apply to bases.

The proportion of the molecules of an acid or other electrolyte which are dissociated in solution is known as the *degree of dissociation or of ionisation* (α).

α may be determined by a number of methods. For example, if the electrical conductivity of an electrolyte is determined for different concentrations it is found that the conductivity divided by the concentration (*equivalent conductivity*) increases to a constant and finite value as the solution becomes more dilute, owing to the increase in ionisation, and the consequent provision of more ions to carry the current. The ratio of the equivalent conductivity of a solution of an electrolyte to its value when the concentration is infinitely small is a measure of α.

Concentration.—It is now time to give the term *concentration* (c) a quantitative meaning. In accordance with the usual expression of normality it will be taken to indicate the number of grm.-equivalents of substance contained in a litre of solution. Conversely, the *dilution* (v) of a solution will be the volume in litres containing 1 grm.-equivalent. A grm.-equivalent is the equivalent weight (compared with hydrogen) of a substance expressed in grms., and $c=1/v$.

Law of Mass Action.—There is another means of arriving at an expression for the strength of an acid or a base. The equation

$$HA \rightleftharpoons H^{\cdot} + A'$$

differs from that given on p. 4 in that the equation sign is here two half-arrows. This indicates that, as we now know, the dissociation is reversible, *i.e.*, the two ions may recombine to form a molecule of acid. The equation therefore represents an equilibrium state in which only a proportion of the acid molecules are ionised, so that in solution there are $H^{\cdot}$ ions, A' ions, and undissociated HA molecules in a state of balance which

may be altered, *e.g.*, by dilution. If the concentrations of these constitutents are represented by $C_{H^{\cdot}}$, $C_{A'}$, and C_{HA} respectively, we have that the rate of ionisation (r_1), according to Guldberg and Waage (1867), is proportional to the active mass (expressed as the concentration) of the unionised acid, and is represented as

$$r_1 \propto C_{HA} = k_1 \,.\, C_{HA},$$

where k_1 is a constant. Similarly, the rate (r_2) of " de-ionisation " (formation of HA molecules) by which the reaction is reversed, is proportional to the number of collisions between the $H^{\cdot}$ and A' ions. This number is obviously proportional to the number of ions—*i.e.*, to their concentrations. Therefore,

$$r_2 \propto C_{H^{\cdot}} \,.\, \text{and} \propto C_{A'},$$

or,

$$r_2 \propto C_{H^{\cdot}} \,.\, C_{A'} = k_2 \,.\, C_{H^{\cdot}} \,.\, C_{A'},$$

where k_2 is another constant.

That r_2 is proportional to the *product* of the concentrations of the ions is obvious if we imagine that the number of $H^{\cdot}$ ions is doubled. The number of possible collisions will then also be doubled. The same applies if the number of A' ions is doubled, and the $H^{\cdot}$ ions kept at their original amount. Now, if *both* are doubled at once, the number of possible collisions will be quadrupled, and since this number is proportional to the concentrations, we see that r_2 is proportional to the product of $C_{H^{\cdot}}$ and $C_{A'}$.

Now, at the point of equilibrium the reaction proceeds at equal rates in both directions, and therefore $r_1 = r_2$, *i.e.*,

$$k_1 \,.\, C_{HA} = k_2 \,.\, C_{H^{\cdot}} \,.\, C_{A'},$$

or,

$$K = \frac{k_1}{k_2} = \frac{C_{H^{\cdot}} \,.\, C_{A'}}{C_{HA}}.$$

This important equation, in which K is the *ionisation constant*, is an expression of the *law of mass action* and serves as a quantitative indication of the strength or degree of ionisation of an acid. It is preferable, however, to express K in terms of α. Now, in the reversible ionisation system represented by the above equation, if C is the concentration of acid and α is the degree of ionisation, then the concentrations of the $H^{\cdot}$ and A' ions produced will each be αC, since equal amounts of each are produced from the same amount of acid. The concentration of the acid remaining unionised is then $(1-\alpha) \,.\, C$. Obviously, if ionisation is complete, $\alpha = 1$, the concentrations of each ion will be C, and that of the undissociated acid will be zero, because none remains unionised. At the other extreme, if there is no dissociation $\alpha = 0$, $C_{H^{\cdot}}$ and $C_{A'} = 0$, but $C_{HA} = C$.

We now substitute the new values in the mass action equation and obtain :

$$K = \frac{(a \,.\, C)(a \,.\, C)}{(1-a) \,.\, C} = \frac{a^2 \,.\, C}{(1-a)}.$$

Expressed in this way K is a direct measure of the degree of ionisation for a particular concentration, and can therefore be determined from measurements of the conductivity of the solution (see p. 6).

Polybasic acids have therefore several values of K corresponding with the ionisation of their hydrogen atoms in successive stages, *e.g.*, for a dibasic acid there are two values :

$$K_1 \ldots\ldots\ldots \quad H_2SO_4 \rightleftharpoons HSO'_4 + H^{\cdot},$$
$$K_2 \ldots\ldots\ldots \quad H^{\cdot} + HSO'_4 \rightleftharpoons SO''_4 + 2H^{\cdot}.$$

Titration of such acids shows that neutralisation may occur in successive stages with the formation of acid salts (*e.g.*, $KHSO_4$), and the case of phosphoric acid is demonstrated on p. 20.

The above reasoning may, of course, be applied to any reversible reaction, as well as to bases and to salts, but the ionisation of a simple acid has been chosen as the example most appropriate for those interested in the measurement of hydrogen ion concentration. With polybasic acids the reasoning is a little more complicated, and this also applies when there are more than three ions or reactants to be considered, or the influence on a reaction of added compounds is sought. The relation is nevertheless extremely useful for the determination of the course and extent of a reaction, and has many applications in practice and theory of which the measurement of hydrogen ions is one example.

The ionisation constants of a number of acids are shown in Table 1, p. 141.

Hydrogen Ion Concentration and Ph Value

Effect of Dilution on Ionisation.—We shall be concerned chiefly with very dilute solutions of electrolytes in which C is therefore very small. Since K is constant $a^2/(1-a)$ will be correspondingly large, *i.e.*, a will approach unity. In other words, ionisation increases as the concentration decreases. Some acids, *e.g.*, hydrochloric acid, are completely ionised in relatively strong solutions such as decinormal ; others, such as organic acids, require dilution to 0·00001N or less strength, while others never ionise completely.

Hydrogen Ion Concentration.—This term has not yet been defined, but it may be brought into line with the definition of normality if it is taken as *the number of grams of active or ionised*

hydrogen per litre of solution. This does not imply that hydrogen ions may be weighed. Their very existence is only hypothetical and this definition is merely a useful means of expression.

A 0·1*N* solution of an acid contains one-tenth of a grm.-equivalent of acid per litre. If the acid is completely ionised each grm.-equivalent will yield one H· ion, so that the hydrogen ion concentration ($C_{H\cdot}$) will be one-tenth of a grm. per litre, or simply 10^{-1}. For 0·01*N* solutions it will be one-hundredth (10^{-2}), and so on. If, however, as is usually the case, the acid is only partly ionised in 0·1*N* solution, and its degree of ionisation is α, then since the hydrogen ion concentration refers only to active hydrogen ions, $C_{H\cdot}$ will be $\alpha \,.\, 10^{-1}$. Similarly for 0·01*N* solutions, when, of course, α will be nearer to unity, and the hydrogen ion concentration nearer 10^{-2}, but actually $\alpha \,.\, 10^{-2}$. In general, for an acid of concentration C, $C_{H\cdot}=\alpha \,.\, C$.

As an example, hydrochloric acid, the strongest acid, is actually ionised to the extent of only 91·4 per cent. in 0·1*N* solutions, and therefore $C_{H\cdot}=0{\cdot}914 \,.\, 10^{-1}$; 0·01*N* solutions are 96·4 per cent. ionised, and $C_{H\cdot}=0{\cdot}964 \,.\, 10^{-2}$.

Acetic acid is a weaker acid, and for 0·1*N* solutions $C_{H\cdot}=0{\cdot}013 \,.\, 10^{-1}$ ($\alpha=1{\cdot}3$ per cent.); for 0·01*N* solutions $C_{H\cdot}=0{\cdot}0417 \,.\, 10^{-2}$.

pH Value.—It will be apparent that the above method of expressing hydrogen ion concentration will prove clumsy when we are dealing with many solutions or if we wish to plot results graphically and include a wide range of concentrations. Sörensen [2] therefore suggested that hydrogen ion concentration should be expressed as *the logarithm of the reciprocal of the hydrogen ion concentration.* This he called the *pH value* (also written $p_{H\cdot}$ or $P_{H\cdot}$), in which p stands for the potential ("potenz"). This important definition is expressed by the equations:

$$\mathrm{pH} = \log 1/C_{H\cdot} = \log 1/\alpha \,.\, C = -\log C,$$

or,

$$C_{H\cdot} = 10^{-\mathrm{pH}}.$$

To divide the hydrogen ion concentration into 1 and take the logarithm of the result may sound like a riddle, but this definition is actually very simple for the reason that it enables us to express the strength of an acid in terms of a simple number and shows at once the relation of a solution to neutrality.

Neutrality.—It has already been shown (p. 4) that neutralisation is associated with the formation of water. Expressed ionically:

$$(H^{\cdot}+A') + (B^{\cdot}+OH') \rightleftharpoons (A'+B^{\cdot}) + H_2O,$$

or simply,

$$H^{\cdot}+OH' \rightleftharpoons H_2O,$$

the $H^{\cdot}$ being contributed by the acid and the OH' by the base. At the neutral point there is an exact balance, and equal numbers of $H^{\cdot}$ and OH' ions are present, *i.e.*, $C_{H^{\cdot}}=C_{OH'}$. Apply the mass action law, and

$$K=\frac{C_{H^{\cdot}} \cdot C_{OH'}}{C_{H_2O}}.$$

But water is only slightly ionised, and since there is a preponderance of unionised H_2O molecules, C_{H_2O}, which is always large relatively to $C_{H^{\cdot}}$ and $C_{OH'}$, is therefore relatively constant. Then

$$K \cdot C_{H_2O}=K_\omega=C_{H^{\cdot}} \cdot C_{OH'},$$

where K_ω, the new constant, is the ionisation constant of pure water and is given by the product of the hydrogen and hydroxyl ion concentrations. But pure water furnishes equal numbers of $H^{\cdot}$ and OH' ions, and so

$$C_{H^{\cdot}}=C_{OH'}=\sqrt{K_\omega}.$$

K_ω has been determined from measurements of the conductivity of "pure" water (see, however, p. 25). It varies with temperature, and its value at 18° C. may be taken as $0{\cdot}59\times10^{-14}$ (or $1{\cdot}04\times10^{-14}$ at 25° C.). For our present purpose it is sufficiently accurate to take the value 10^{-14}, whence

$$C_{H^{\cdot}}=C_{OH'}=\sqrt{10^{-14}}=10^{-7}.$$

This means that 1 litre of water contains 10^{-7} grm.-equivalents of hydrogen ions (*i.e.*, 10^{-7} grm. of $H^{\cdot}$), and 10^{-7} grm.-equivalents of OH' ions (*i.e.*, 17×10^{-7} grm. of OH'). Here, again, the need is apparent for the logarithmic artifice to transform clumsy figures, and following the definition of pH value, we have

$$pK_\omega=\log 1/K_\omega=\log 1/10^{-14}=\log 10^{14}=14,$$

or,

$$pH=pOH=7.$$

We have thus arrived at the important result that *the pH value of pure water, or the pH at neutrality, is 7.*

This enables us to define the degree of neutrality in terms of the pH scale.

(*a*) If $C_{H^{\cdot}}$ is greater than $C_{OH'}$ the pH will be less than 7, and the reaction will be acid.

(*b*) If $C_{H^{\cdot}}$ equals $C_{OH'}$ the pH will be 7, and the reaction will be neutral.

(*c*) If $C_{H^{\cdot}}$ is less than $C_{OH'}$ the pH will be greater than 7, and the reaction will be alkaline.

Alkaline Solutions.—It remains now only to explain the position in the scale of alkaline solutions. We have chosen

acids to illustrate our argument merely because in our minds we probably instinctively think of acids before bases. The whole argument applies equally to bases as to acids, $C_{OH'}$ being substituted for $C_{H^{\cdot}}$ throughout, and *vice versâ*.

Thus it is plain that even bases have a hydrogen ion concentration, just as acids have an hydroxyl ion concentration, but that these concentrations are smaller than the hydroxyl and hydrogen ion concentrations in the two cases respectively. In the case of a base the pH value is easily found from the pOH value, since pH = 14 − pOH. For example, sodium hydroxide is a strong base, and therefore finds a place on the alkaline side of the pH scale approximately as far removed from neutrality as hydrochloric acid is on the acid side. Actually a 0·1*N* solution has $C_{H^{\cdot}} = 8{\cdot}6 \times 10^{-14} = 10^{13{\cdot}07}$. This means either (*a*) 1 litre contains only 0·000,000,000,000,086 grm. of hydrogen ions; (*b*) its pH value is 13·07; (*c*) its pOH value is (14 − 13·07) = 0·93. The great convenience of the pH scale may now be appreciated.

The pH Range.—All aqueous solutions, and we are concerned only with these, contain $H^{\cdot}$ and OH' ions derived from the water even if the dissolved substance does not supply either. The presence of acids, bases, or other electrolytes in varying quantities may increase or decrease the actual numbers of the ions present, so that it is apparent that on either side of pH 7, the neutral point, we may have an infinite range of solutions of different pH values. How far does this range extend? On the acid side the highest $H^{\cdot}$ concentration possible at ordinary temperatures is found in 6*N* hydrochloric acid which has pH = −0·3. The conception of a negative pH value loses all its terrors if we remember that the pH value itself is a negative logarithm, and that log 1 = 0. On the alkaline side, 7*N* potassium hydroxide solution has $C_{H^{\cdot}} = 3{\cdot}3 \times 10^{-15}$ (pH 14·5, pOH −0·5), which is the lowest possible $H^{\cdot}$ concentration and highest OH' concentration.

The pH scale, therefore, extends from about −0·3 to 14·5, and is represented in Fig. 2, which also shows the relative positions on the scale of a number of common liquids and solutions.

FIG. 2.—IMPORTANT PH VALUES.

Acid.		Alkaline.	
1·0	0·1*N* hydrochloric acid.	7·07	NEUTRALITY. Nitrobacter. Soil nitrification organisms. Diastase (potato or pancreas), Peroxydase, Catalase, or Oxydase (vegetables or liver). Lipase (serum). Papain. Urease (soya bean). Trypsin (yeast). Saliva. Hops.
1·4	Pepsin (stomach).		
1·8	Gastric juice. *Aspergillus* limit.		
1·9	Zirconium hydroxide precipitates.		
2·0	Whey.		
2·2	Lemon juice.		
2·5	Cherry juice. Invertase (*Asp. niger*).	7·1	*B. amylobacter. Azotobacter.*
2·8	Vinegar. Wine.	7·5	Catalase (blood). Blood. Urine.
3·0	Orange juice. *Th. thiooxydans.* Vinegar. Sucrose inversion. 0·1*N* acetic acid.	7·0	Milk. *B. stutzeri.*
		7·7	Defecation and sulphitation of sugar.
3·1	Rhubarb juice.	7·8	Erepsin (yeast or intestines). *Nitrosomonas.*
3·2	Grape juice.	8·0	*Th. denitrificans. B. subtilis.* Pancreatic enzymes. Trypsin (yeast). Quinhydrone electrode limit. Skin.
3·4	Pineapple juice. Strawberry juice.		
3·5	Diastase and Invertase (*Asp. niger*).		
3·6	*B. para typhi.* agglomerates. Wine.	8·2	Sea water.
3·9	Beer.	8·3	Trypsin (pancreas). Erepsin (intestine). Pancreatic juice.
3·97	0·05*M* Potassium hydrogen phthalate.		
4·0	Pineapple juice. Orange juice. Malt protease. Invertase (potato). Pepsin and Zymase (yeast). Lipase (gastric juice). Fungi spore germination. Optimum dye absorption. Vinegar. Skin.	8·4	Sea water.
		8·5	*B. pycnoticus.* Sea water. Defecation and sulphitation of sugar. Tap water.
		8·6	Bean juice. Lipase (serum).
		8·8	Beet juice.
		9·0	Pancreatic enzymes.
4·2	Tomato juice. Apple juice. Plum juice. Least acid reaction for stable beer.	9·2	0·05*M* Borax.
		9·3	Trypsin (pancreas).
		9·5	Potato juice.
		10·0	Arginase (liver). Catalase, Peroxydase, and Oxydase (vegetables).
4·3	Fruit pectase.		
4·4	Diastase (malt). Emulsin. *B. typhi.* agglomerates. Invertase (yeast).	11·0	0·1*N* ammonia.
		13·10	0·1*N* sodium hydroxide solution.
4·5	Pepsin (yeast).		
4·6	Banana juice. Iso-electric point of casein.	14·5	7*N* potassium hydroxide solution.
4·7	*B. coli* limit. Beer. Iso-electric point of gelatin.		
5·0	*Pneumococcus* agglomerates. Beer wort. Cucumber juice. Invertase (potato or yeast). Lipase (gastric juice). Papain.		

	Acid.	Alkaline.
	Saliva. Beer wort in copper. Malt. Sarcina. Urine. Gastric juice. Hops.	
5·2	Bean juice. Beer wort in mash tun.	
5·3	Yeast carboxylase.	
5·4	*Aspergillus niger*.	
5·5	Raw cane juice. Diastase (*Asp. niger*). Optimum for sizing of paper. Plant cells.	
5·7	Yeast limit. Malt.	
5·8	*B. putrificus*. *Mucor glomerula*.	
6·0	Potato root and beet juices. Flour. Diastase (potato or saliva). Rennet (stomach). Zymase (yeast). Beer wort. Distilled water. Pure paper. Sarcina. Barley in cold water.	
6·2	Carboxylase (yeast). Pineapple sap.	
6·4	Tap water, less CO_2.	
6·5	*B. coli*. *B. vulgare*. Flour.	
6·6	Milk. Maltase (beer yeast).	
6·8	Muscle juice. Maple juice. *B. pyocyaneum*. Tap water.	
7·07	NEUTRALITY (" pure " water).	

NOTES.—Where one pH value only is given for an organism or enzyme this represents the optimum value. Where two are given, these represent the extreme values of the range, which in the case of organisms is usually 3 or 4 pH units. The values must be regarded as approximate, since they will vary to some extent according to the origin, which in the cases of enzymes is given in brackets. Precipitation pH values of metal hydroxides are given in Table 3, p. 143.

Other means of expressing the pH range have been devised,[3] but that above is the most usually accepted method, and is probably the most convenient. One worker has suggested that the neutral point be considered zero, and acidities and alkalinities reckoned as positive and negative pH values respectively, from 1 to 7. The relation of a medium to neutrality is thus denoted by (pH − pOH), since at the neutral point this equals zero.

The Relation of pH and C_H.—This is shown in the table below (p. 14), but a few additional hints may be given for rapid

calculation, since in this work it is a great advantage to be able to think at will either in terms of normality or of pH value.

Since $pH = \log 1/C_{H^\cdot}$, or $C_{H^\cdot} = 10^{-pH}$, we have, for example,

$$\text{if } C_{H^\cdot} = 10^{-4\cdot5},\ pH = 4\cdot5.$$

If we have a $0\cdot001N$ solution of an acid which is completely dissociated,

$$C_{H^\cdot} = 0\cdot001 = 1/1000 = 10^{-3},$$

and,

$$pH = \log 1/10^{-3} = 3.$$

If the solution is $0\cdot005N$,

$$C_{H^\cdot} = 0\cdot005 = 5/1000 = 5 \times 10^{-3},$$

and

$$pH = \log 1/5 \times 10^{-3} = \log 10^3/5 = \log 10^3 - \log 5 = 3 - \log 5 = 2\cdot33.$$

Klopsteg [4] has made this calculation the basis of a table for the rapid determination of pH from $C_{H^\cdot}$ and *vice versâ*. The same purpose is served equally well by using the following relations in conjunction with the table of logarithms on p. 148.

If $pH = x\cdot yz$,
then $C_{H^\cdot} = [\text{antilog } (1 - yz/100)] \times 10^{-(x+1)}$; *
or, conversely, if $C_{H^\cdot} = a \times 10^{-b}$,
$pH = b - \log a$.

It should be noted that *an increase in pH value corresponds with a decrease in hydrogen ion concentration and an increase in hydroxyl ion concentration*, because the higher the pH value the more alkaline is the solution. If the pH decreases by 1 unit, the $C_{H^\cdot}$ is multiplied by 10.

The table below shows the relation of pH, $C_{H^\cdot}$, $C_{OH'}$, and normality (C) for a fully dissociated acid and base. If the acid or base is not fully dissociated, $C_{H^\cdot} = \alpha \,.\, C$.

Acid Range.			Normality of acid or base (C).	Alkaline Range.		
$C_{H^\cdot}$	$C_{OH'}$	pH		pH	$C_{OH'}$	$C_{H^\cdot}$
10^{-0}	10^{-14}	0	$1\cdot0N$	14	10^{-0}	10^{-14}
10^{-1}	10^{-13}	1	$0\cdot1N$	13	10^{-1}	10^{-13}
10^{-2}	10^{-12}	2	$0\cdot01N$	12	10^{-2}	10^{-12}
10^{-3}	10^{-11}	3	$0\cdot001N$	11	10^{-3}	10^{-11}
10^{-4}	10^{-10}	4	$0\cdot0001N$	10	10^{-4}	10^{-10}
10^{-5}	10^{-9}	5	$0\cdot00001N$	9	10^{-5}	10^{-9}
10^{-6}	10^{-8}	6	$0\cdot000001N$	8	10^{-6}	10^{-8}
10^{-7}	10^{-7}	7	Neutrality	7	10^{-7}	10^{-7}

* For example, the pH of "pure" water (p. 10) is 7·07. Then $C_{H^\cdot} = [\text{antilog } (1 - 7/100)] \times 10^{-(7+1)} = (\text{antilog } 0\cdot93) \times 10^{-8} = 8\cdot51 \times 10^{-8}$.

It should be remembered that the pH notation applies without adjustment to the cases of acid or bases containing more than one available H atom or OH group respectively (*e.g.*, H_2SO_4, $Ba(OH)_2$, H_3PO_4, etc.). Thus, there is no question of dividing by 2 or 3 as in the calculation of quantities for normal solutions, because here we deal only with the concentration of ionised hydrogen ($H^{\cdot}$), whilst the normality of a solution is an expression of the concentration of the dissolved substance in terms of the weight equivalent to 1 grm.-atom of hydrogen, without regard to ionisation. Similarly the pH of a solution of an oxidising or reducing agent bears no relation to its oxidising or reducing powers, whereas the normality expresses its concentration in terms of that of the active constituent.

It is useful for the determination of the strengths of acids to deduce a relationship between pH, pK, and α. We saw (p. 8) that $K=\alpha^2 . C/(1-\alpha)$. But since $C_{H^{\cdot}}=\alpha . C$, $K=\alpha . C_{H^{\cdot}}/(1-\alpha)$, or $1/C_{H^{\cdot}}=\alpha/K . (1-\alpha)$. Therefore $pH=\log 1/C_{H^{\cdot}}=\log 1/K+\log \alpha/(1-\alpha)$, or, $pH=pK+\log \alpha/(1-\alpha)$.

Table 1 (p. 141) gives pK for a number of acids and bases.

Hydrolysis.—It is apparent that the hydrolysis of a salt into an acid and base in aqueous solution is really a reversal of the neutralisation reaction.

$$BA+H.OH \rightleftharpoons B.OH+HA \rightleftharpoons B^{\cdot}+OH'+H^{\cdot}+A'.$$

Four cases arise :—

(*a*) *B.OH and HA are both strong.*—They will then both be fully ionised in dilute solutions, and since there will be equal concentrations of both $H^{\cdot}$ and OH' ions the solution of such a salt will be neutral (pH 7), and the hydrolysis negligible (*e.g.*, potassium chloride).

(*b*) *B.OH is weak and HA is strong.*—Here there will be hydrolysis, but the solution will be acid, because of the excess of $H^{\cdot}$ ions (*e.g.*, calcium chloride).

(*c*) *B.OH is strong and HA is weak.*—Such salts are hydrolysed to give alkaline solutions (*e.g.*, sodium carbonate).

(*d*) *B.OH and HA are both weak.*—Small quantities of $H^{\cdot}$ and OH' ions may both occur, so that the solution may be neutral or almost neutral as in (*a*) ; but undissociated acid and base will always remain (*e.g.*, ammonium acetate).

The pH of a solution of a salt therefore depends on the ionisation constants of the acid and base constituting it or produced by hydrolysis. These above four cases are further illustrated by the following section.

Titration Curves [5].—The behaviour of an acid or base on neutralisation is shown very clearly by *titration-* or *neutralisation-curves.* In the case of an acid the amount of standard alkali

added is plotted as abscissa, and the pH value of the resulting mixture as ordinate. For typical acids and bases curves such as those shown in Fig. 3 are obtained. It is assumed in each case that 10 c.c. of standard acid is being titrated with standard alkali of the same strength.

Curve AXB represents the neutralisation curve of a strong acid by a strong base. It will be seen that in the neighbourhood

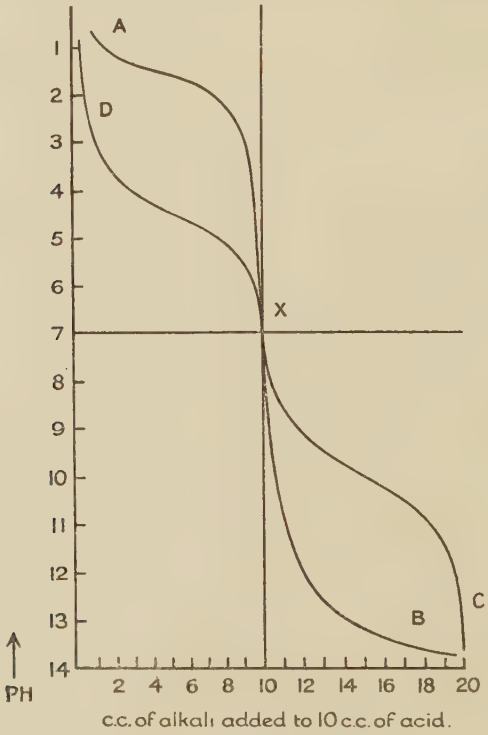

FIG. 3.

of the equivalence point (*i.e.*, when 10 c.c. of alkali have been added) the pH changes very rapidly from about 3 to 11 on the addition of about 2 c.c. of alkali. The mid-point of the straight vertical portion of the curve, therefore, corresponds with neutrality, in this case pH 7 at X.

Curve DXB, the lower half of which is coincident with that of AXB, would be obtained with a weak acid and a strong base. In this case the mid-point of neutrality is displaced towards the

region of alkalinity (lower portion of the curve, about pH 8) and the change in pH on the addition of alkali is not so rapid in the neighbourhood of this point as in the above curve. Conversely, curve AXC is the neutralisation curve of a strong acid by a weak base. The pH of neutrality is about 6, and the salt formed reacts acid in solution.

Curve DXC is that from a weak acid and weak base. The pH at neutrality may be 7, but it does not change rapidly with addition of alkali, and the salt has therefore the properties of a *buffer* (see p. 20).

Now the effect of a salt having an anion in common with an acid is to repress the ionisation of the latter when the two are mixed, and the concentration C_{HA} of unionised acid may be taken as equal to that of the total acid. But if the salt is highly ionised at the mid-point of the neutralisation range (half-transformation point) when equivalent amounts of acid and salt are present, $C_{HA}=C_{A'}$, and therefore the ratio $\alpha/(1-\alpha)$ in the equation on p. 15 becomes equal to unity. Since $\log 1=0$,

$$pH=pK.$$

At the point of exact neutrality the pH value is therefore numerically equal to pK (see Table 1, p. 141).

It is plain that neutralisation curves show what is happening in an acid-base mixture, not only at the end-point, but throughout the titration. In addition, they enable an accurate determination to be made of the end-point itself, and their shape is a useful indication of the nature and properties of the salt produced. Their use is not limited to the simple cases described above, but may be extended to polybasic acids, to salts which ionise in several stages (cf. Fig. 4, p. 20), and to mixtures of acids, the discussion of which is outside the scope of this work. The practical side of the subject is dealt with on p. 107.

The use of titration curves is not restricted to neutralisation reactions. Such curves are most useful for the determination of end-points in oxidation-reduction and other titrations, where the visual method is open to a big personal error. They are the basis of electrometric titration.[6]

Finally, it should be noted that the end-point of a titration is not necessarily at the neutral point pH 7. The actual pH is dependent on the nature of the acid and base concerned.

Limitations of the Theory

Many of those interested in the practical aspects of the measurement of hydrogen ions have not had the opportunity of keeping abreast of the controversy that for some years has

raged around the theory on which it is based, and the author feels that in fairness to such workers the limitations of the above theory should be pointed out.

In the first place, the law of mass action applies to the " active masses " of the reactants, and we have assumed that the active mass equals the molecular concentration. This is legitimate enough for weak electrolytes and in dilute solutions (*e.g.*, less than 0·01*N*), but it involves the assumption that the molecules are " free," and themselves occupy no volume. It has been found, in fact, that strong electrolytes in concentrated solutions do not obey the law of mass action. G. N. Lewis [7] has therefore introduced the " activity " (a), a purely arbitrary factor, by which the concentration is multiplied to make it satisfy the law of mass action. Thus, for the reaction $A+B \rightleftharpoons C+D$,

$$K=\frac{a_C \cdot a_D}{a_A \cdot a_B}$$

Activity has no definite numerical value ; it is merely a correction, which is determined by experiment and varies according to the electrolyte. If we were strictly accurate, therefore, we should replace pH by paH($=\log 1/aC_{H^+}$), where a is the activity coefficient. Debye and Hückel,[7] also, have deduced a somewhat complicated equation which contains a number of unknowns not easily determined, and though applicable to a number of strong electrolytes is still not entirely free from criticism. It is based on the assumption that ionisation is always complete, but that each negative ion in solution is surrounded by a " region " containing an excess of positive ions, and *vice versâ*. Other workers have modified it by the introduction of quantities which allow for influences such as those of the undissociated molecules in the solution. Even so, their modifications do not hold universally and are very complicated.

Those ignorant of the latest advances in electrochemistry need not be perturbed by the thought that these new and complex theories exist.[7] In the first place, they deal only with the exceptional cases of concentrated solutions and strong electrolytes. For dilute solutions the correction is very small, *e.g.*, for Sörensen's standard mixture (0·01*N* HCl + 0·09*N* KCl) the difference between pH and paH is only 0·04.

Secondly, so long as we realise that when we measure pH values we are really measuring the paH, it does not matter how we express our results. Measurements are always compared with those made on standard reproducible solutions, and the expression of these measurements in terms of the pH value as originally defined is therefore open to no objection, although not strictly accurate. As a matter of fact it is still an open question whether some of the effects attributed to H^+ ions (*e.g.*, hydrolysis of esters)

are not determined by their concentration rather than by their activity.[8]

Another type of objection is put forward by antagonists of the ionic theory. According to E. H. Armstrong,[7] water consists of groups of OH_2 or " hydrone " molecules in complex and varied forms, and built up according to the equation $x\mathrm{H_2O}+\epsilon\delta=(\mathrm{H_2O})_x+\epsilon\delta$; $\epsilon\delta$, the electrolytic determinant, prevents the reversal of the reaction. Chemical changes are thus reversed electrolyses :

$$\mathrm{A_2}+\epsilon\delta+\mathrm{B_2}\rightleftharpoons\mathrm{AB}+\mathrm{AB}+\epsilon\delta.$$

With reference to these and similar theories, it can only be pointed out here that the ionic theory as described above has proved so invaluable in both theoretical and practical physical chemistry that, even if we admit that it is not all that can be desired, there is no object in abandoning it for a less satisfactory theory. At the same time we must keep its limitations in mind, and be prepared to consider alternatives or modifications. At present, however, in common with most other chemists, the author prefers not to depart from the rendering of the theory given above.

Buffer Solutions

We have dealt hitherto with compounds which have either a neutral or a markedly acid or alkaline reaction. But, in addition, there is a very important class of compounds which possess the properties of both acids and bases. These are known as *regulators* or *buffers*,* and their importance rests in their power to resist change in pH on the addition of acid or alkali.

These substances are salts of weak acids or bases, or mixtures of weak acids or bases with their salts. Weak acids themselves are slightly ionised, and if in addition anions are contributed by the presence of a salt, their ionisation is still further repressed, though the salt is itself greatly dissociated. Similar considerations apply to mixtures of weak bases and their salts.

On what does the regulating or buffering effect of these mixtures depend ? Suppose a strong acid is added to the salt of a weak acid or base. The $H^{\cdot}$ ions it produces will unite with the anions (A') of the salt to give molecules of an acid which is so weakly ionised that the pH will be almost unchanged. If a strong base is added, the OH' ions unite with the cations ($B^{\cdot}$) of the salt to form a weak base, which, again, is weakly ionised, and there is therefore no change in pH. In other words, buffers remove the $H^{\cdot}$ ions of acids or the OH' ions of bases and form, respectively, weak acids or bases which are so slightly ionised that the pH value is unaffected.

* " *Buffer* " is the English rendering of " *puffer*," the German translation of the term " *tampon* " (plug or bung), suggested by Fernbach in 1900.

Let us consider the neutralisation curve of a weak acid by a weak base, since the salt so produced will be a buffer. This is shown by the curve DXC in Fig. 3 (p. 16), from which it is obvious that over the range of the almost flat portion of the curve from D to X and X to C the addition of alkali to the mixture produces little change in pH. The mid-points of these ranges are the points at which the buffer action of the salt is greatest.

The salts of phosphoric acid are excellent buffers, and Fig. 4 is the titration curve of 50 c.c. of 0·1*N* phosphoric acid with

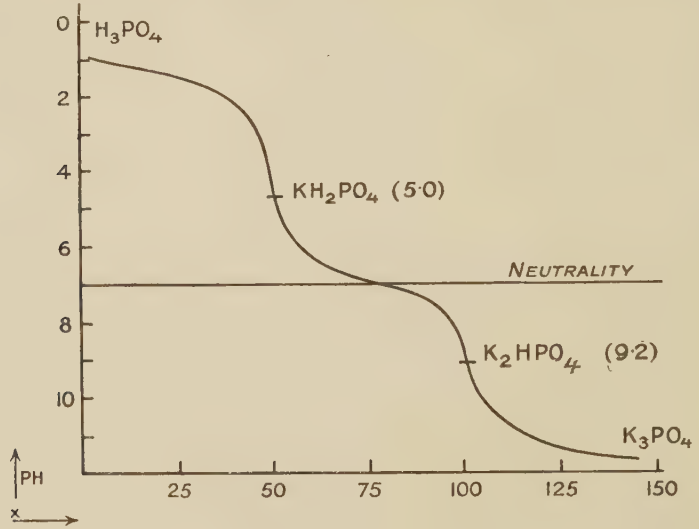

FIG. 4.

0·1*N* potassium hydroxide solution. The almost vertical portions of the curve at pH 5 and 9·2 represent the formation of the acid and basic phosphates, KH_2PO_4 and K_2HPO_4, respectively, and it is apparent that the best buffer action will be obtained with mixtures of the two.

The most important buffer substances are acetates, borates, citrates, phosphates, and phthalates. A number of buffers occur in nature in the form of complex organic compounds, while amino-acids, peptones, beef broth, malt extract, gelatine, etc., have similar properties. These substances are usually *amphoteric* (*ampholytes*), *i.e.*, they possess both acidic and basic properties, and therefore may act as a base in acid solutions or as an acid

in alkaline solutions. Hence their capacity of removing H˙ and OH′ ions, and thereby of resisting a change in pH. Their mode of ionisation may be expressed thus :

$$\underset{\text{(Acidic.)}}{H^{\cdot}+R.OH} \rightleftharpoons H.R.OH \rightleftharpoons \underset{\text{(Basic.)}}{RH+OH'}.$$

The organic ampholytes are of great importance in biology. Amino-acids, which contain both acidic (—COOH) and basic ($-NH_2$) groups, are an example (p. 116).

To demonstrate the resistance of buffers to pH change it may be mentioned that if 1 c.c. of 0·1*N* hydrochloric acid solution is added to 1 litre of distilled water (pH 7), the pH of the resulting liquid will be 4—*i.e.*, that of a 0·0001*N* solution of a strong acid. If, however, it is added to a 1 per cent. peptone solution of pH 7, the resulting pH is about 6·9—*i.e.*, hardly changed.

Buffer Value.—It is useful to be able to define the buffering properties of a particular solution quantitatively. Of the numerous expressions suggested that of Van Slyke is most practicable :

$$\pi = d\text{B}/d\text{pH}.$$

π is known as the *buffer value*,[9] and is a measure of buffering power in terms of *the number of gram-equivalents of strong acid or alkali required to produce a change of one unit in the pH value of the buffer.* The quantity dB is therefore the amount of acid or base added (in grm.-equivalents/litre), and dpH is the resulting change in pH value. Thus $\pi = 1$ when the addition of 1 grm.-equivalent of acid or base per litre causes a change in pH of 1 (*i.e.*, $d\text{B} = d\text{pH}$). By plotting π against the pH the maximum values of π obtained give the pH for which the buffer is most suitable. Complex buffers may therefore be investigated by this method.

Practical Buffer Solutions

In general, it may be said that the properties of a buffer depend on the chemical nature of the buffer substance and of the acid or alkali added, and on their positions on the pH scale. Buffers, therefore, should be chosen which are most efficient in the neighbourhood of the pH value corresponding with the dissociation constant of the acid or base concerned.

As Part III. on the colorimetric method will show, buffers play an important part in the measurement of hydrogen ion concentration. The choice of suitable buffers is therefore a matter of great importance and will be determined chiefly by convenience, by the purity of the materials available, and by the

nature of the solution concerned. Thus, for example, activated charcoal will adsorb hydrogen ions, and therefore act as a buffer, but it is hardly convenient for practical purposes.

For most general purposes the standard solutions suggested by Clark and Lubs [10] are to be recommended. It is true that the mixtures prepared by Sörensen [2] have been very accurately standardised, but their primary constituents are substances which cannot always be obtained in a pure state, whilst potassium chloride and biphthalate, and boric acid, the essential constituents of the Clark and Lubs mixtures, are marketed in this country in the state of purity necessary for the purpose. Table 2, on p. 142, gives the compositions of a range of these solutions extending from pH 1·0 to pH 10·0. Solutions the pH values of which have been questioned are asterisked. The effects of temperature are small. Thus, 0·05*M* potassium hydrogen phthalate has a pH of 3·02 at 18°–30° C., which rises only to 3·94 at 50°–60° C. For the little-used range, pH 10 to 12, the buffers suggested by Kolthoff [6] and by Ringer [6] may be recommended.

Purity of Reagents. A few practical notes on this subject are desirable, since even small traces of impurity may upset the pH value of the buffer.

Hydrochloric acid.—The preparation of a 0·2*N* solution presents no difficulties. *Sodium hydroxide* solution, however, may prove a source of trouble in accurate work on account of the presence of sodium carbonate, and the procedure suggested by Newbery [10] has been found useful.

Solutions in 200 c.c. of boiling water of about 32 grms. each of barium hydroxide $Ba(OH)_2.8H_2O$ and sodium sulphate $Na_2SO_4.10H_2O$ are mixed while boiling and diluted to exactly 1 litre. The precipitated barium sulphate is allowed to settle, and the top liquor, which contains the sodium hydroxide, titrated and adjusted to 0·2*N*. For ordinary colorimetric measurements this solution is quite suitable, but for highly accurate work the barium hydroxide should be freed from carbonate by recrystallisation of a hot saturated solution, and care taken that the sodium sulphate has not lost water of crystallisation. The solution is decanted into a paraffin-lined bottle [prepared by rapidly rinsing the bottle with molten paraffin wax] with a good rubber stopper. Air containing carbon dioxide should be excluded from the solution as far as is possible, and if a stock solution is likely to be required it should be kept in a burette fitted with a soda-lime tube. As a rule, however, this is unnecessary.

Potassium hydrogen phthalate ($HOOC.C_6H_4.COOK$) may be prepared by the method of Dodge,[11] or the special product sold for the purpose used. If the latter is not available the purest salt obtainable should be recrystallised twice at 25° and

dried at 112°. Dissolve 40·836 grms. per litre for a 0·2*M* * solution.

Potassium (or sodium) dihydrogen phosphate [12] (KH_2PO_4) for use in buffers is also sold. Alternatively the commercial salt may be recrystallised twice from water and dried at 112° till constant in weight. The loss on ignition should be 13·23 per cent. *Disodium hydrogen phosphate* ($Na_2HPO_4,2H_2O$) is purified if necessary by recrystallisation twice, and dried to constant weight over calcium chloride. There should be a loss of 25·28±0·1 per cent. on ignition. *Sodium carbonate* is best obtained [13] by heating sodium bicarbonate or oxalate for one hour at 360°. *Potassium chloride* is recrystallised from water four times (once if pure), and dried at 120°. For the 0·2*M* solution dissolve 14·912 grms. per litre.

Boric acid.—The commercial product, recrystallised from water three times and dried between filter papers and over calcium chloride, is suitable. Dissolve 12·4048 grms. in 1 litre of the 0·2*M* potassium chloride solution. Ordinary distilled water may be used throughout.

Other useful buffer ranges have been suggested, *e.g.*, by Palitzsch [14] and by McIlvaine,[15] but those given above are considered suitable for most purposes. Reference, however, must also be made to Kolthoff's buffers,[6] because no acid or base is required for their preparation. They consist of mixtures of succinic acid or primary potassium phosphate with borax, and cover the range pH 3–9. All these solutions provide for pH values in 0·2 steps, but it is obvious that 0·1 steps may be obtained with sufficient accuracy by taking the necessary intermediate quantities.

Universal Buffer.—Prideaux and Ward [16] have prepared a mixture of equivalent amounts of phenylacetic, phosphoric, and boric acids in quantities such that a solution in 1 litre of water is 0·1*N* to the whole mixture, but 0·02*N* to each hydrion.† If v is the number of c.c. of 0·2*N* hydrochloric acid or sodium hydroxide, which, when it is added to 100 c.c. of the above buffer solution and the mixture diluted to 200 c.c. gives the required pH, then

$$pH = 3{\cdot}1 \pm 0{\cdot}1185v.$$

* A 1·0*M* solution contains the molecular weight in grms. of substance dissolved in a litre of water, whilst a 1·0*N* solution contains the equivalent weight in grms. of active constituent per litre. Thus, in the case of potassium permanganate the *N* solution is calculated on the available oxygen, whereas the *M* solution is obtained from the molecular weight. We speak of a *M* solution of, say, sodium chloride because in such cases normality has no real meaning.

† The British Drug Houses, Ltd., London, sell tubes containing sufficient of the mixed acids to make 1 litre of solution.

The — sign refers to the acid and the + sign to the base, and for convenience the expression may be plotted in the form of a curve relating pH and v. These buffers cover the range pH 2·7–11·4, and though unstable in glass vessels and not highly accurate, are useful for many purposes. Their properties depend on the fact that the ionisiation constants of the acids differ by relatively short stages (see Table 1, p. 141), and the effects of the various acids therefore overlap during neutralisation. Phenylacetic and boric acids have dissociation constants midway between the first and second, and second and third dissociation constants of phosphoric acid, respectively.

In conclusion it should be pointed out that the pH values of buffer solutions are determined by standardisation by means of the electrometric method (p. 27). Though this is usually unnecessary for Clark and Lubs' solutions, it is advisable in cases where the purity of the materials is suspect. Further considerations on the use of buffers and their stability are discussed in connection with the colorimetric method (p. 89).

Water as a Buffer.—Since water is our most common solvent and plays a rather exceptional part as far as the ionisation theory is concerned, a few words must be devoted to it.[18] According to our definition of neutrality as equilibrium between equal numbers of $H^{\cdot}$ and OH' ions (p. 10), we have inferred that water, which dissociates into these ions only *

$$H_2O \rightleftharpoons H^{\cdot} + OH',$$

represents the standard of neutrality. Now, when the law of mass action was applied to this equation (p. 10) we obtained the relation

$$K_\omega = C_{H^{\cdot}} \cdot C_{OH'},$$

or,

$$pK_\omega = pH + pOH = 14.$$

We see that water, our standard of neutrality, has from the ionic point of view both acidic and basic properties, but that these are balanced. Distilled water contains no salts, and therefore has no buffer effect. It is therefore affected more readily than any other liquid by small amounts of impurity which may produce large changes in pH value. Alkali from glass containers is a possible contamination, though atmospheric carbon dioxide is far more serious. Thus if distilled water is allowed to take up as much carbon dioxide from the air as it will hold (0·3 per cent. by volume) its pH will fall to about 5·7, *i.e.*, it will become acid. This happens so readily that really

* See, however, p. 19. The possibility of other ions being produced from water must not be forgotten, but need not interfere with our deductions.

" pure " water may be said to be non-existent, and determinations of K_ω have had to be made under the most stringent conditions for the elimination of as much impurity as possible. Those of Kohlrausch and Heydweiller [17] are usually accepted, but are not entirely free from criticism.[18] They show, however, that the pK of water changes from 14·93 at 0° to 12·24 at 100°, and that the ionisation is so small that it occurs to the extent of only one molecule in 555,000,000.

Pure water, therefore, although the theoretical standard of neutrality for measurements of pH value, is too poor a buffer for practical purposes. Actually, however, this poor buffering power is an advantage, since it means that on the addition of distilled water to a salt or buffered solution apart from the effect of dilution, the pH value of the latter will be unchanged. If water were a good buffer its presence would obviously upset the pH of solutions prepared from it or with which it was mixed.

Distilled Water.—The pH value of distilled water will depend on its method of preparation and storage.

Van der Hoeven [19] obtained a value of 6·6–7·0 for freshly distilled water. This seems high, since Canals and Mousseron,[20] who used a pyrex glass still and stored the water in the presence of platinum black, obtained a value of 5·5–6·0. Matthews [21] showed that whilst distilled water supersaturated with carbon dioxide had pH 4·4, the value rose to 5·1 after shaking. The pH of ordinary distilled water (5·9) rose only to 6·0 after boiling. Kolthoff has also determined the pH of distilled water. He shows that since equilibrium between water and air is reached only slowly, storage vessels should be kept full and well-stoppered. It should also be noted that the bad buffering power of water renders the methods for measuring its pH value open to criticism (see Kolthoff,[18, 22] and p. 135).

These remarks are introduced as of general interest, since the pH value of the distilled water used will not influence the results. Tap water or other natural waters which contain salts should not, of course, be used.

Acid Taste.—It was mentioned at the outset (p. 5) that acid taste is one of the criteria of the strength of an acid. We have now advanced far enough in our explanation of true acidity to modify this statement. Certainly in fruit juices the pH and acid taste may be correlated with the strengths of the acids present (Lvov [23]), but in addition to the effect of the hydrogen ion we have often to allow for the modifying or even antagonistic effect of the anion.

Berlatzky and Guevara [24] have shown that the limiting concentrations of acid for which acid taste is perceptible are sulphuric

2·9, nitric 3·2, citric 3·9, tartaric, hydrochloric, and lactic 4·3, acetic 4·5, phosphoric 4·7. This order by no means follows the strengths of the acids. Harvey [25] pointed out that apples and tomatoes of the same pH had different degrees of sourness. With weakly acidic and poorly buffered solutions the degree of sourness may be influenced by the digestive juices (see also p. 126).

Summary of Chapter I

Acids and bases are dissociated (ionised) in aqueous solutions with the formation of positively charged $H^{\cdot}$ ions and negatively charged OH' ions respectively, to extents depending on their strengths. This strength is expressed by the ionisation constant. The concentration of $H^{\cdot}$ or OH' ions is most conveniently expressed as pH or pOH, where $pH = \log 1/C_{H^{\cdot}}$. Neutrality is represented by pH 7 at which pH = pOH, and this is the pH value of theoretically pure water.

Solutions which resist change in pH value are known as buffers, and mixtures to cover any desired range may be prepared from salts.

The complete acid properties of a system may therefore be summed up in terms of :

(*a*) The really effective acidity or hydrogen ion concentration (pH), which determines to what extent a solution will behave in a manner characteristic of acids. This is distinct from

(*b*) the potential acidity or actual concentration in grm.-equivalents of acid present as determined by titration.

(*c*) The buffering effect.

In the measurement of hydrogen ions we are concerned principally with the measurement of (*a*), and to a less extent with that of (*c*), whilst the measurement (*b*) is the acidimetry or alkalimetry of volumetric analysis.

CHAPTER II

CHOICE OF METHODS FOR THE MEASUREMENT OF HYDROGEN ION CONCENTRATION

Methods Available.—Numerous methods are available for the determination of pH values,[26] but with two exceptions these are of theoretical interest only. The two exceptions with which we are concerned are:

(1) *The Electrometric Method.*—In this case a cell is made up of two half-cells, the potential or voltage of one of which is a constant and known. The potential of the other is dependent on the pH value of the solution (*i.e.*, the solution to be examined) in which it is placed, so that if the voltage of the combination is measured, the pH value of the solution is obtained by subtracting the potential of the standard half-cell from that of the whole. To measure the potential of the unknown half-cell directly might appear more convenient, but for the reasons set out in Part II. this is not practicable.

(2) *The Colorimetric Method.*—The solution to be examined is mixed with a suitable indicator, and the colour obtained compared with the colours of a series of mixtures of the same indicator with buffer solutions of known pH values. The buffer solution which gives the same colour as the test solution has the same pH value.

Choice of Methods.—Of the two methods, the electrometric method is the more accurate and must always be considered as the final appeal in doubtful cases. At the same time it may itself be open to suspicion in certain cases, though these have been fully investigated (see p. 67), and there is no reason why the beginner should fall foul of them. The technique is more difficult than in the case of the colorimetric method, but again it is not beyond the capacity of an intelligent worker who is familiar with the fundamentals of electricity. The apparatus, however, is rather expensive and "home-made" electrical instruments are not all that can be desired. At the same time, in the present description of the method the possibility of limited resources has always been kept in mind. The procedure also is often long and the apparatus takes some time to set up.

It is for these reasons that the colorimetric method is often preferred in spite of the fact that it is less accurate, and that the matching of colours introduces a considerable personal factor. The technique is simple, little or no special apparatus is required, and once the solutions are prepared the measurements may be carried out very rapidly. Pitfalls for the unwary exist, of course, but are by no means so troublesome as in the electrometric method.

General Conclusions.—For routine purposes, therefore, where the accuracy required is not of the highest order (say 0·1–0·2 pH), the colorimetric method may be recommended. But where only a few measurements are to be made at a time, with perhaps a few weeks' interval between, it is preferable to use the electrometric method rather than to prepare fresh standard solutions for each measurement. The electrometric method should be used for checking purposes, especially of buffer solutions, and is indispensable where an accuracy of 0·1–0·01 pH is required. In most of the applications of hydrogen ion concentration, therefore, the colorimetric method is used, even if it has to be standardised against the electrometric method for the solution concerned, and a predetermined correction applied.

Finally, there are certain cases which are discussed in the chapters on the methods concerned, in which there is no alternative but to use one particular method. For example, it is obvious that it is not possible to match colours if the solution itself is originally highly coloured or turbid, and unless some artifice is adopted for eliminating or removing the colour or haze without altering the pH of the solution the electrometric method must be used. On the other hand, certain substances in solution upset the measurements of the potential of the unknown half-cell, and if these are present the colorimetric method will give more reliable results. One great advantage of the colorimetric over the electrometric method is that it may be easily adapted to overcome the problems which arise in particular cases. There are very few solutions, however, for which neither method can be used, even if it is possible only to obtain an approximate result (accurate to 0·1–0·2 pH). The beginner, therefore, need not be deterred by the apparent limitations of the methods, as it is easy to determine which method will prove most suitable in a particular case, and there are a number of artifices for overcoming difficulties.

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PART II

THE ELECTROMETRIC METHOD

CHAPTER I

OUTLINE AND THEORY OF THE METHOD

As already explained (p. 27), the principle of the method depends on the measurement of the voltage of a cell, this voltage being dependent on the hydrogen ion concentration of the liquid (*i.e.*, the test solution) used in the cell. An outline of the theoretical basis of the method is given in the following pages, and a close study of these is desirable for the proper understanding of the method and of the formulæ used for the calculation of the pH value.

Normal Electrode Potentials

Solution Pressure.—When a solid is placed in a liquid (*e.g.*, a piece of metal in water) it tends to dissolve. This tendency may be very small and not detectable by ordinary methods, but it is nevertheless present. From the analogy of the tendency of water to be transformed by evaporation into water-vapour, this tendency to dissolve is termed the *solution pressure*. Thus, the solution pressure of sugar is large, and that of platinum is small. To particularise, if a metal is placed in an aqueous solution of one of its salts, say zinc in zinc sulphate solution, it will tend to dissolve by virtue of its solution pressure and therefore to increase the number of zinc ions already in the solution. On the other hand, the zinc ions already in solution produced by ionisation of the salt will tend to deposit on the zinc and so resist the solution pressure of the latter. There are, therefore, two opposing forces, the solution pressure (P) of the metal, and the " deposition pressure " (p) of the metal ions. The pressure p exerted by ions in solution is, of course, their *osmotic pressure*, or the pressure which must be exerted on the solute (dissolved substance) to prevent it expanding so as to occupy a larger volume of solution (*cf.* gaseous pressure).

Metal ions are positively charged, and therefore in this case positive ions will tend to enter the solution from the metal and

leave the latter negatively charged, until the accumulation of positive electricity in the solution resists further change.

The three possibilities are shown in Fig. 5. (*a*) If P is greater than p the metal sends ions into solution until this is resisted, and the metal and solution become negatively and positively charged respectively. Example, zinc in zinc sulphate. (*b*) If P equals p (an exceptional case) no change occurs, and both metal and solution are electrically neutral. (*c*) If P is less than p, the positive metal ions in solution deposit on the metal, making the metal positive and leaving the solution negative. Example, copper in copper sulphate. A little consideration will show that these possibilities are quite consistent with the ionisation theory (Part I.), since the anions which have lost their cation partners account for the negative charge in the solution. The positive

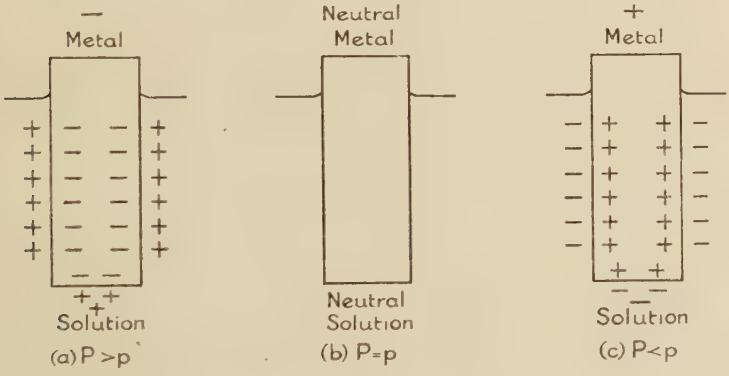

FIG. 5.

and negative ions may be imagined to attract without completely neutralising each other, and so to form an electrical double layer in the immediate neighbourhood of the electrode, as shown in Fig. 5. The condenser effect of this double layer is the seat of the electrical energy of the electrode. Actually, it is about 1 molecule thick.

We have seen that the solution pressure of a metal depends (1) on its electrical state with respect to the solution, and (2) on the osmotic state with respect to the solution. It should, therefore, be possible to express one of these determining conditions in terms of the other. This is easily achieved by calculating the maximum work obtainable when 1 grm.-molecule of metal is changed from the pressure P to the lower pressure p as in the case of zinc, where $P > p$. This may be done in two ways.

(1) *Electrical work.*—It has already been shown (p. 3) that 96,540 coulombs are associated with the dissolution of 1 grm.-equivalent of metal, so that for 1 grm.-molecule of metal of valency n the quantity of electricity is $96,540 . n$ coulombs. Electrical work is given by the product volts × coulombs, in this case $96,540 . n . e$, where e is the voltage (*i.e.*, electrode potential, see below).

(2) *Osmotic work.*—Provided the change is reversible, *i.e.*, it can go with equal facility in either direction, one can easily deduce from the laws of dilute solution that the osmotic work gained is $RT \log_e P/p$, where R is the gas-constant * and T the absolute temperature.

These are different expressions for the same amount of work and may now be equated, whence

$$96,540 . n . e = RT \log_e P/p.$$

If we now convert R (which equals 1·99 calories) into electrical units by Joule's factor 4·183, and the natural logarithms into ordinary logarithms by the factor 2·3026, we have :

$$e = \frac{RT}{96,540 . n} \log_e \frac{P}{p} = \frac{2·3026 \times 1·99 \times 4·183}{96,540 . n} . \log_{10} \frac{P}{p}$$
$$= \frac{0·0001983T}{n} . \log \frac{P}{p}.$$

e is called the *electrode potential* of the metal, and is a measure of the potential or electrical difference between the charges on the metal and those in solution. It is positive for metals such as zinc [see (*a*) and above], and negative for copper [see (*c*)] since P is less than p, and $\log P/p = -\log p/P$.

Effect of Concentration.—In the case (*a*), Fig. 5, an increase in concentration of zinc ions in the solution increases the tendency to deposit and to neutralise the negative charge on the metal, *i.e.*, the electrode potential is lowered. In the case of copper (*c*) there will be a tendency to render the positive metal still more positive, and so e will increase.

Now the gas-laws * applied to dilute solutions state that $P . v = R . T$ or pressure $= R . T/v$. Since $v = 1/c$ (see p. 6), $P = c . R . T$. If this expression of pressure in terms of concentration is applied to P and p in the above equations, R and T cancel out, and we have :

$$e = \frac{0·0001987T}{n} . \log_{10} \frac{C}{c} . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

* The gas laws are a combination of Boyle's and Charles' laws and state that for a gas, pressure × volume/absolute temperature = constant (R). If the pressure is measured in grms./cm.^{2} and the volume in c.c., then R is expressed in grms. × cms. and is 84,760. This equals 83,150,500 ergs or 1·99 calories. Since E is in volts, R must be multiplied by 4·183 to obtain its value in volt-coulomb (*i.e.*, electrical) units.

where C and c are the concentrations of ions corresponding with the solution-pressure and the osmotic pressure respectively. The latter is simply the concentration of the electrolyte, and for the sake of giving the former a meaning it may be considered as the concentration of metal ions in the immediate neighbourhood of the metal electrode. The significance of C is made clearer by rearranging (1), when

$$e = 0{\cdot}000198 \,.\, T/n \,.\, \log C - 0{\cdot}000198 \,.\, T/n \,.\, \log c.$$

Now, if the metal is immersed in a $1{\cdot}0M$ solution of its ions, $c=1$ and the second term vanishes because $\log 1 = 0$. Then

$$e \text{ becomes } e_0 = 0{\cdot}000198 \,.\, T/n \,.\, \log C. \quad . \quad . \quad (2)$$

e_0 being called the *normal electrode potential* of the electrode, or the potential it will assume in a $1{\cdot}0M$ solution of its ions, *i.e.*:

$$e = e_0 - 0{\cdot}000198 \,.\, T/n \,.\, \log \,.\, c \quad . \quad . \quad . \quad . \quad (3)$$

It should be noted that e always has the sign of the metal to which it refers. In the present instance ($P > p$) this is zinc and e is negative. For copper ($P < p$), and it is positive. This important equation gives the relation betweeen the actual electrode potential, its normal potential, and the concentration of the solution, without including the quantity C.

Electromotive Force

Electrolytic Cells.—Up to now we have considered only single electrodes, which can, however, by themselves produce no energy. Nevertheless, they have a potential source of work defined by e and seated in the condenser effect of the ionic double-layer (Fig. 5).

Suppose (Fig. 6) we have two such electrodes of opposite character, zinc in zinc sulphate (negative) and copper in copper sulphate (positive), the solutions being separated by the porous division A which allows a current to pass but will not allow the solutions to mix. This constitutes a *voltaic* or *electrolytic cell*—the Daniell cell, in fact. Equilibrium is attained when the double layers are formed and the electrodes are oppositely charged and exert their own characteristic potentials. If the electrodes are now joined by a wire, their opposite charges neutralise one another through it, or in other words, a current passes. At the same time, in the solution there will be a tendency to re-establish the equilibrium, *i.e.*, more zinc will dissolve and more copper will be deposited, and the neutralisation of the charges by means of the current will therefore continue.

E.M.F.—The voltage of an electrolytic cell is called its *electromotive force* (*E.M.F.*), and is the net electrical effect of the two electrodes in combination. In the case of the Daniell cell it is the sum of the electrode potentials, since these are of opposite

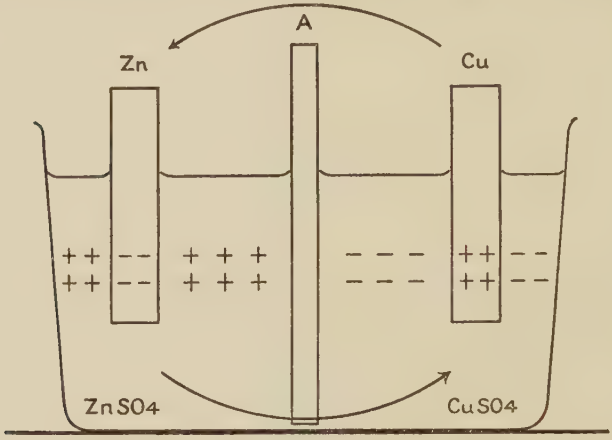

Fig. 6.

sign. This is represented by the distance E (1·1 volts) in Fig. 7 (*a*), the distances E_{Cu} and E_{Zn} from the line of zero *E.M.F.* representing the potentials (0·6 and −0·5 volts respectively) of these electrodes. When, however, both electrodes have the same sign, *e.g.*, zinc and cadmium or copper and silver (Fig. 7 (*b*)), the

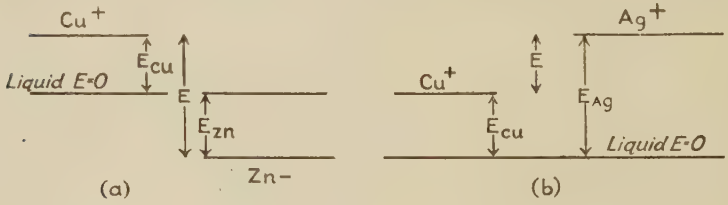

Fig. 7.

E.M.F., or their net effect in combination, is obviously obtained by subtracting their electrode potentials. Table 3 (p. 143) shows the single potentials of a number of elements and radicals in solutions containing 1 grm.-equivalent of their ions.

Concentration Cells.—Suppose now we have two zinc electrodes in solutions of zinc sulphate of different concentrations c_1

and c_2. Then $n=2$ and $e_1=e_0-0{\cdot}000198\,.\,T/2\,.\log\,c_1$, and $e_2=e_0-0{\cdot}000198\,.\,T/2\,.\log\,c_2$. Therefore,

$$E=e_1-e_2=0{\cdot}000198\,.\,T/2\,.\log c_1/c_2 \quad . \quad . \quad (4)$$

Such an arrangement is known as a concentration cell, and the above equation gives its *E.M.F.* (E) in terms of the concentrations of the solutions constituting the electrodes.* If the concentration of one of these is known, that of the other may be found by measuring E for a particular temperature, and it will now be seen how the above formulæ may be applied to the measurement of hydrogen ion concentration.

Standard Electrodes

For reasons which will be apparent later, it is not convenient in practice to use as a standard half-cell a simple electrode consisting of a metal in contact with a solution of one of its salts.

Calomel Electrodes.—The calomel electrode is the standard most frequently employed. The method of preparation is described fully on p. 42, but the electrode consists essentially of a vessel in which a layer of mercury is covered with a paste of mercury, calomel, and potassium chloride solution, and filled up with either $0{\cdot}1M$, $1{\cdot}0M$, or saturated potassium chloride solution. The electrical connection is made by a platinum wire dipping in the mercury. The potentials of half-cells of this type have been studied very thoroughly, and the directions given on p. 42 should enable a calomel electrode to be made whose potential differs little from the values given in Table 4, p. 144. Such a half-cell will maintain a constant potential over very long periods, and when combined with another half-cell may be used to determine the potential of the latter.

Hydrogen Electrode.—So far we have considered only metal electrodes. But by means of a simple device, the potential of a gas such as hydrogen in a solution of its ions may also be measured. As a matter of fact the so-called *hydrogen electrode* is the most usual means of measuring the concentration of hydrogen ions.

The gas electrode is made possible by the fact that a metallic electrode such as platinum coated with a layer of the same finely-divided, spongy metal, will adsorb the gas and behave analogously to a metal electrode when immersed in the solution of electrolyte containing ions from a solution of the gas.

In the case of hydrogen the metal is usually partly immersed in the solution and pure hydrogen bubbled round it until the

* Actually there is also a small potential-difference at the liquid junction (see p. 38), but this is neglected for the moment.

electrode is "saturated." A constant potential is set up after about 5–7 mins., and can then be measured. The electrode produced may be described as that of a piece of "metallic hydrogen" and is completely reversible with respect to the ionisation equation $H_2 \rightleftharpoons 2H^{\cdot}$. Thus, the hydrogen gas may go into solution and become ionised (left to right), or hydrogen ions may be deposited as gas when positive electricity passes from solution to metal (right to left).

Thus, a hydrogen electrode-concentration cell might be either (*a*) two hydrogen electrodes in solution of acids of different hydrogen ion concentrations; or, (*b*) two hydrogen electrodes in the same solution containing gas at different pressures. In this case the pressures, which are proportional to the concentrations of hydrogen ions in the respective solutions, tend to equalise, and hydrogen is ionised on the high pressure side and deposited as gas on the low pressure side. Other gas electrodes (*e.g.*, of oxygen or chlorine) may also be prepared, but a great deal of work has been carried out on the standardisation of the hydrogen electrode.

Other standard electrodes, such as Bijlman's quinhydrone electrode [1, 2] (the preparation of which is described on p. 47 in another connection), have also been suggested as standards. The calomel and hydrogen electrodes, however, are almost universally employed.

Expression of Electrode Potentials.—(1) The absolute value of the potential of a metal electrode may be determined by a number of methods (*e.g.*, by the dropping electrode or the capillary electrometer [3]) which do not, however, come within our scope. They usually depend on the use of an electrode in which means are adopted to obtain zero potential between the metal and solution. It is more usual to express electrode potentials in terms of an easily reproducible reference electrode.

(2) Ostwald suggested the calomel electrode for this purpose, and there is a certain amount of theoretical justification here, since it is probable that the values obtained do not differ greatly from the real single electrode potentials. Such values are termed "absolute" (Palmaer [3]).

(3) Nernst [4] refers potential differences to the hydrogen electrode in a *N* solution of hydrogen ions. This is an arbitrary but more convenient standard, in spite of the difficulty of preparing a standard solution whose strength is accurately normal. The usual procedure is, in fact, to make the actual measurements with the calomel electrode, and then by adding or subtracting the potential of the latter to translate them to the hydrogen electrode standard.

To define the standard of zero potential, to which all other potentials are referred, we may therefore say that *the potential*

difference between a hydrogen electrode under unit pressure (1 *atmosphere*) *of hydrogen, and a hypothetical normal solution of* $H^{\cdot}$ *ions, is zero at all temperatures.* Hence e_0 in equation (3) on p. 33 becomes zero, and since $n=1$ and $pH=\log 1/C_{H^{\cdot}}$, for the hydrogen electrode $e=-0{\cdot}000198 \,.\, T \,.\, \log\, C_{H^{\cdot}}=0{\cdot}000198 \,.\, T \,.\, \log\, 1/C_{H^{\cdot}}=0{\cdot}000198 \,.\, T \,.\, pH$.

Measurement of Hydrogen Ion Concentration

The Cell.—Consider the type of hydrogen concentration cell (*a*) suggested on p. 36, in which the electrodes dip in solutions of different hydrogen ion concentrations c_1 and c_2. Then the *E.M.F.* obtained from equation (4) is

$$E.M.F.=0{\cdot}000198 \,.\, T.\, \log\, c_1/c_2,$$

since the valency (n) of hydrogen is unity. Now suppose that c_2 is the concentration of hydrogen ions we wish to measure, and that the other electrode is the normal hydrogen standard defined above. Then $c_1=1$ for the normal solution and $E.M.F.=0{\cdot}000198 \,.\, T \,.\, \log\, 1/c_2=0{\cdot}000198 \,.\, T \,.\, pH$, since $pH=\log 1/C_{H^{\cdot}}$ (see p. 9).

The pH of the solution corresponding with the concentration c_2 may therefore be calculated from the *E.M.F.* of the above concentration cell and the absolute temperature. But, as pointed out above, measurements in practice are made with the calomel electrode as standard in place of the concentration cell electrode c_1, so that the electrode potential ($e_{cal.}$) of the calomel electrode must be subtracted from the *E.M.F.* (E) obtained in this way. Thus $E.M.F.=E-e_{cal.}$ and the equation becomes:

$$E.M.F.=E-e_{cal.}=0{\cdot}000198 \,.\, T \,.\, pH,$$

or,

$$pH=\frac{E-e_{cal.}}{0{\cdot}000198 \,.\, T} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This important equation will be used for the calculation of all pH values, and should be known by heart. In other words, the potential (in volts) of the calomel electrode at the temperature of the experiment is subtracted from the measured voltage of the hydrogen-calomel electrode cell and divided by the product of 0·000198 and the absolute temperature T (*i.e.*, 273+ordinary temperature in °C.). Values of $e_{cal.}$ at various temperatures are given in Table 4 on p. 144. Various devices for the rapid calculation of pH from this equation also are described later (p. 72).

The actual cell will thus consist of (*a*) a calomel electrode, (*b*) a hydrogen electrode placed in the solution to be tested, and

(*c*) a liquid to join up the two electrode solutions. This combination is expressed shortly thus, Pt,H_2, test solution | connecting solution | calomel, Hg.

It is obviously important that the pressure of the hydrogen inside the hydrogen electrode should equal that of the atmosphere (760 mm.) or the calculation will be complicated by the introduction of a correction for the effect due to the pressure-concentration cell of the type (*b*) mentioned on p. 36. In practice this is usually easily ensured, though for highly accurate work the following corrected formula (Clark and Lubs [5]) may be used:

$$pH=(E+E'-e_{cal.})/0{\cdot}000198\,.\,T,$$

where E' is the correction for the hydrogen pressure (P_{H_2}) and equals $R\,.\,T/F\,.\log 1/P_{H_2}$. A decrease in pressure corresponds with a decrease in electrolytic solution pressure, and the electrode becomes more positive. The expression for E' is obtained from the formula $E=2R\,.\,T/F\,.\log P'_{H_2}/P_{H_2}$, when $P'_{H_2}=1$, *i.e.*, when comparison is made with a hydrogen electrode under 1 atm. pressure. In such circumstances a correction should also be made for the pressure of the external surrounding atmosphere if this differs greatly from 760 mm.

The Connecting Liquid.—To make electrical connection it is necessary that the two electrode solutions be joined by some medium which conducts electricity. If the two are placed in direct contact a complication is introduced into the above equation owing to the fact that a small potential is always set up where two liquids of different nature or concentration meet, on account of the diffusion of the ions from one into the other. This *diffusion potential* depends on the rate of travel of the ions, and once set up remains constant. It may easily be calculated for a concentration cell containing liquids of concentration c_1 and c_2 and equals $[(u-v)/(u+v)]\,.\,0{\cdot}000198\,.\,T\,.\log c_1/c_2$, where u and v are the mobilities of the cation and anion respectively. The value obtained is added to or subtracted from the measured *E.M.F.* according to its sign. This formula holds only under "ideal" conditions, *e.g.*, when ionisation is complete, the boundary sharp, and there is an ion present common to both electrodes. Unless, therefore, one employs a flowing junction of the type suggested by Lamb and Larson [6] to ensure absolute reproducibility, it is preferable not to make a correction, but to insert an intermediate liquid which will eliminate the diffusion potential. As a matter of fact this latter alternative is nearly always used for pH measurements, and a saturated solution of potassium chloride, one of the constituents of the calomel electrode, is the best form of "bridge." Its influence depends on the fact that the $K^{\cdot}$ and Cl' ions have almost equal mobilities, and if a fresh junction is made for each measurement and the readings taken quickly, no correction need be made.

Bjerrum[7] suggested the use of $3{\cdot}5M$ potassium chloride as a bridge solution. This does not, however, completely eliminate diffusion potentials, and in accurate work the *E.M.F.* is measured with both $3{\cdot}5M$ and $1{\cdot}75M$ bridge solutions of potassium chloride, and the correction found by subtracting the values obtained. Other bridge solutions (*e.g.*, potassium or ammonium nitrates) are not so convenient for pH measurements, and the prevention of diffusion by membranes, etc., is not advisable as the electrical contact produced is poor and the *E.M.F.* is not always attained rapidly.

Summary

A metal or hydrogen electrode placed in a solution containing its ions exerts a potential, owing to the tendency to dissolve or deposit, which is dependent on the concentration of those ions. This potential can be determined by linking the electrode or half-cell with one of known potential, and by measuring the voltage (electromotive-force) of the complete cell produced. Electrode potentials are always *expressed* in terms of the potential of the hydrogen electrode in a N solution of hydrogen ions at atmospheric pressure. They are actually *measured*, however, against the calomel electrode, and the potential of the latter subtracted from the *E.M.F.* of the cell obtained. Corrections must be applied for pressures above or below 1 atmosphere, and for changes in *E.M.F.* due to diffusion, though it is preferable to eliminate these effects completely by the use of suitable apparatus. For pH measurements the *E.M.F.* of the combination, hydrogen electrode in the solution of $H^{\cdot}$ ions to be tested | potassium chloride bridge | calomel electrode, is used, and the pH of the solution at t° C. is given by $(E - e_{\text{cal.}})/0{\cdot}000198\,.\,(t^{\circ}+273)$.

In conclusion,[8] attention must again be drawn to the limitations of the ionic theory mentioned on p. 17. The arbitrary nature of what we have taken as zero potential, viz., the potential of the normal hydrogen electrode, should be remembered, and in the calculation of H ion concentration (or pH) from E, the possibility that we are dealing with H ion "activity" should be borne in mind. The arguments as outlined above, however, lead to formulæ whose practical use is beyond question, and the worker outside the fields of theoretical electrochemistry will do well to make them the foundation of his work on pH measurements.

CHAPTER II

PREPARATION OF THE ELECTRODES AND CELLS

Calomel Electrodes

The calomel electrode is the reference electrode and care should therefore be taken that the materials used for its preparation are pure. Pure calomel and distilled mercury are now sold for the purpose, but where they are not obtainable the following notes (Findlay [9]) may be of assistance.

Mercury [10].—Zinc and lead are first oxidised to a scum by bubbling air through the mercury for several hours. It is then filtered through a pinhole in a filter paper, or squeezed through a clean dry bag of closely-woven cloth. It is then again filtered, shaken for 20 minutes with a solution of mercurous nitrate in dilute nitric acid, well washed with distilled water, and dried by filter-paper. Finally, it is allowed to fall in fine droplets, produced by means of a funnel with a drawn-out stem (A), through a column B of acid mercurous nitrate solution contained in a tube of the shape shown in Fig. 8, where C is a bent capillary tube (1 mm. diameter). C is first filled with a little pure mercury, and the solution added. Pure, dry mercury will issue from D as fast as it enters at A, the amount in the bend remaining constant.

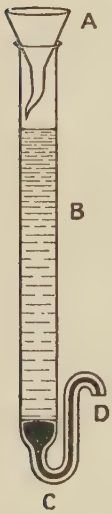

Fig. 8.

Calomel.—If the electrolytic method described by Lipscomb and Hulett [11] is not used, calomel of the required purity may be prepared by dissolving the purified mercury in distilled nitric acid in the presence of excess mercury, and adding the dilute acidic solution to distilled hydrochloric acid, the first third of the distillate from which has been rejected. The precipitated calomel is washed free from acid by decantation, and after filtration on a Büchner funnel, is dried. An excess of mercury should be present throughout. Calomel of the required purity is, however, easily obtainable.

Potassium Chloride.—This should be recrystallised from a saturated solution in water, and the crystals filtered and dried

in a steam oven. The strength of the solution to be used is discussed below.

Electrode Vessel.—In its simplest form this consists (Fig. 9) of an ordinary 4-oz. bottle with a wide neck fitted with a rubber stopper through which pass (1) the inlet tube A, the upper end of which is attached by rubber tubing, supplied with a clip, to the potassium chloride reservoir B ; (2) the tube C, in the lower

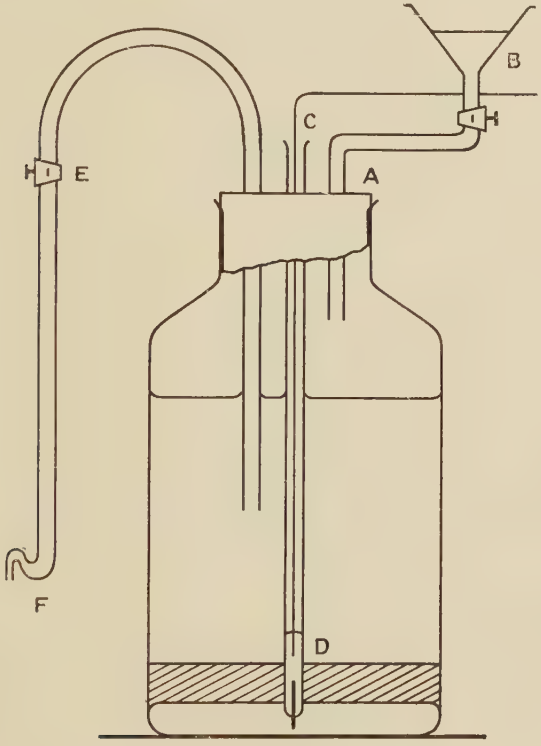

FIG. 9.

end of which is sealed a piece of platinum wire * so that about 5 mm. project into the vessel and 5 mm. remain inside and under the mercury layer D ; (3) an outlet tube E, bent and drawn out as shown so that the outlet end is 1–2 mm. in diameter. The

* Platinum wire may be sealed in glass [12] by almost closing the end of the glass tube, inserting the wire and completely sealing it in a hot flame. By blowing gently down the open end of the tube the thick glass round the seal is then thinned out a little. The chance of cracking subsequently is minimised if the seal is well annealed in the luminous flame.

portion F can be joined by rubber-tubing at a point below the level of the liquid inside the bottle, so that it may be removed and cleaned. Connection is made with the rest of the apparatus by means of a piece of copper wire, the end of which is scraped bright and amalgamated by rubbing it in with little mercury. It passes down the tube C and dips in the mercury covering the platinum wire.

Preparation of the Electrode.—The apparatus is carefully cleaned and dried, the stopper and tubes fitted in, and sufficient mercury added through A to cover the projecting platinum wire, and about 5 mm. of the sealed end of C. A paste is then prepared by rubbing together in a clean mortar calomel, mercury, and an excess of the potassium chloride solution (see below). The solution is decanted after a few minutes, the process repeated twice, and a layer of the paste run in carefully over the mercury, care being taken that it does not touch the platinum wire. A large volume of potassium chloride solution is then saturated with the paste that remains and run in slowly through A by means of a pipette until the bottle is almost full. The reservoir B is then filled with the remainder and connected to A. The outlet tube E is filled by removing F and carefully sucking over the solution by means of rubber tubing attached in its place. The clip is closed and F replaced. The latter may be flushed out between experiments, and so freed from contamination, by opening the clip.

The electrode should not be used for a day or so after it has been prepared, and, so long as it is not unduly disturbed, should maintain its proper potential indefinitely. It should always be given time to assume the temperature at which measurements are being made.

Potassium Chloride Solution.—Three types of calomel electrode are used according to the strength of the potassium chloride solution, which may be 0·1*M*, 1·0*M*, or saturated. The choice is largely a matter of individual preference. The saturated solution has the disadvantage of the highest temperature coefficient, *e.g.*, its potential falls 7 millivolts between 18° and 30° C. It also tends to creep badly and to crystallise round the open end of the tube F. The author [13] prefers it, nevertheless, to the other solutions, especially where a " bridge " of the same solution is used, for it is easily and accurately prepared, and is least affected by changes in concentration due to diffusion. Moreover, its high conductivity enables a low-resistance galvanometer to be used. A little of the solid should be placed in the bottom of B to keep the solution saturated in case of a rise in temperature, while the "creeping " difficulty is easily overcome by the judicious application of vaseline at likely points, or by emptying F.

The mercury is positive to the solution, and the potentials of the three electrodes are tabulated for various temperatures on p. 144 (Table 4).

Hydrogen Electrode

Apparatus.—There are almost as many patterns of hydrogen electrode as there are workers on the subject. The writer's experience, however, is that no useful object is served by multiplying examples, and it is proposed only to describe the simplest

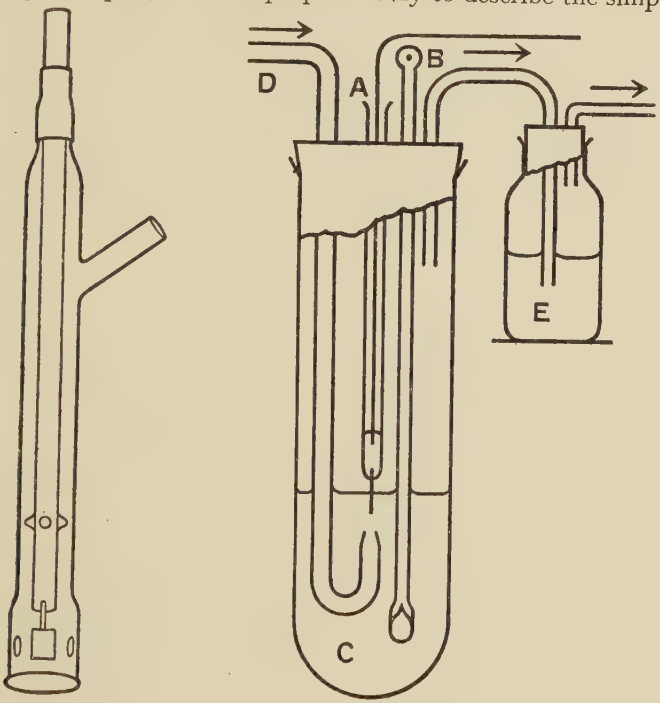

Fig. 10.

types which have been found most useful for general purposes. One of the great advantages of simplicity is that cleaning is facilitated. Special forms of electrode designed for particular classes of work will be found in the literature or among the special methods (Part IV.).

Fig. 10 (*a*) shows Hildebrand's modification of Sand's hydrogen electrode.[14] It consists essentially of a central tube in which is sealed a piece of platinum wire about 1·5 cm. long,

of which about 1 cm. projects, while the inside portion is connected by a layer of mercury with an amalgamated copper wire as in the case of the calomel electrode (p. 41). By means of a rubber band, this is fitted tightly into the neck of the outer tube, which is provided with a side-inlet for the hydrogen, while the lower end is bell-shaped, and dips in the liquid to be tested. It may be held in a clamp which slides on a vertical rod, and is adjusted so that the liquid almost covers the wire, and washes it up and down without completely exposing it, when the hydrogen enters at the side tube and bubbles out under the bell. Holes are also provided in the sides of the bell to enable the solution to assume its natural level.

Some workers prefer as an electrode a small sheet of platinum foil or gauze about 1 sq. cm. in area. This may easily be welded to the wire by placing the two pieces in contact in the required position, raising them to white heat in the blow-pipe, and giving the joint a sharp blow on an anvil with a small hammer. The

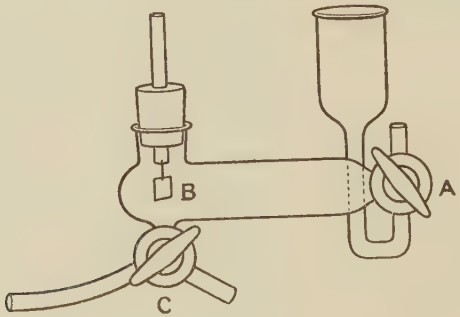

Fig. 11.

writer, however, advises the wire type, as it is easier to prepare and clean, while it attains equilibrium rapidly, and is not so readily poisoned.

Fig. 10 (*b*) shows another simple electrode, made from a boiling-tube, and useful when the test liquid must be protected from the air. The waste hydrogen bubbles through a water-trap E. A is the electrode, B a themometer, and another tube (not shown) makes connection with the potassium chloride bridge. Fig. 11 shows Clark's rocking electrode,[15] which is widely used in America, particularly for certain biological and soil studies in which the use of unstable liquids renders it essential that rapid equilibrium is attained (Hasselbach [16]). The vessel is connected with the calomel electrode through the closed bottom tap C, which also runs to waste, and is filled with hydrogen

by means of the 3-way tap A on the right. The solution is then run in through the funnel connected with the latter till the vessel is one-third full. A closed and rapid equilibrium is attained by rocking or shaking the vessel so that the platinum B is alternately covered and exposed, and only the thin film of liquid remaining on it has to be saturated by the gas. Two such electrodes are usually connected to the same calomel electrode and mounted so that a cam driven by a small motor, or the device suggested by Cameron and Shearer,[17] gives them a rocking motion without churning.

Platinisation of the Electrode.—The platinum wire must now be coated with a layer of platinum black sufficient to hide the metallic lustre yet not thick enough to render the electrode sluggish. This operation is important, for on it depends the efficiency of the electrode as a means of catalytically promoting the change of molecular to atomic hydrogen and thence to hydrogen ions.

FIG. 12.

The wire is gently scraped and cleaned by immersing it for a few minutes in warm aqua regia. It is washed, placed in a 2 per cent. solution of platinic chloride containing a trace of lead acetate, and connected to the negative terminal of a 6-volt battery of accumulators. A piece of platinum, connected to the positive terminal, is also placed in the solution. Vigorous gas evolution occurs, and after 40 seconds the terminals are reversed for 30 seconds, and then finally returned to their original polarities for another 40 seconds. The wire should then have a velvet or jet-black appearance. Both electrodes are washed, the platinic chloride replaced by 10 per cent. sulphuric acid, and electrolysis continued, with the prepared electrode as cathode (*i.e.*, connected to the negative terminal), for 5 minutes. This removes traces of chlorine. The deposit must not be injured by the touch, nor should it be allowed to dry, and the writer keeps his electrodes, when not in use, in narrow glass tubes (Fig. 12) sealed at one end, and filled with distilled water. These are conveniently stored, with the amalgamated connecting wire in position, in thermometer cases.

To strip the electrode, the bulk of the wet deposit is first wiped off with a piece of clean soft cloth, and the wire finally brightened up with aqua regia. If for any reason the electrode behaves in a suspicious manner, it should be replatinised at once, as unsatisfactory results will be obtained sooner or later. The effect of " poisons " on the electrode is discussed on p. 67.

Hydrogen.—By far the most convenient source of hydrogen

is that sold compressed in cylinders. It should be passed through a wash-bottle containing an alkaline 2 per cent. solution of potassium permanganate, and this will serve also to regulate the rate of flow to about 2 bubbles per second before the electrode is connected up. Where this hydrogen is not available a Kipp apparatus containing pure zinc and sulphuric acid may be used, but the hydrogen must be bubbled in succession through wash-bottles containing solutions of potassium hydroxide, mercuric chloride, alkaline pyrogallol, and alkaline potassium permanganate, and finally dried over a layer of phosphorus pentoxide. Hydrogen prepared by electrolysis (at 0·8 amp.) of a $4N$ solution of sodium hydroxide or of saturated baryta, with a gold cathode and nickel anode, yields a purer product if oxygen is eliminated by enclosing the cathode in a bell-shaped vessel. The gas is passed over calcium chloride to dry it, and traces of oxygen then removed in a tube containing platinum gauze at 400°.[18]

Quinhydrone Electrode [19]

Theoretical.—Quinhydrone is a slightly soluble, crystalline equimolecular compound of quinone and hydroquinone. In solution it is ionised into these two compounds of which quinone ($C_6H_4O_2$) is not further ionised, whilst hydroquinone ($C_6H_4(OH)_2$), which is a dibasic acid, gives two H ions. Thus:

$$[C_6H_4O_2,C_6H_4(OH)_2] \rightleftharpoons C_6H_4O_2+C_6H_4(OH)_2,$$

and

$$C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2+2H^{\cdot}.$$

In other words, if a metal electrode is placed in a solution of quinhydrone, a potential difference is set up as the result of the reduction of quinone to quinhydrone by the hydrogen ions.

From equations 1 and 3 (p. 32), and the Law of Mass Action (p. 7), it follows from the above equation that

$$E=e_0-R\,.\,T/2F\,.\log C_{C_6H_4(OH)_2}/C_{C_6H_4O_2}\,.\,C_{H^{\cdot}}\,.\,C_{H^{\cdot}}$$
$$=e_0-R\,.\,T/2F\,.\log C_{C_6H_4(OH)_2}/C_{C_6H_4O_2}-R\,.\,T\,./2F\,.\log[1/C_{H^{\cdot}}]^2.$$

If, however, the pH of the solution is below about 8, the hydroquinone is only slightly dissociated, and since its concentration then equals that of the quinone, $C_{C_6H_4(OH)_2}=C_{C_6H_4O_2}$, and the second term in the equation disappears because $\log 1=0$. Since, further,

$$\tfrac{1}{2}\log[1/C_{H^{\cdot}}]^2=\log 1/C_{H^{\cdot}}=\text{pH},$$
$$\therefore\ E=e_0-R\,.\,T/F\,.\,\text{pH}=e_0-0{\cdot}000198\,.\,T\,.\,\text{pH}.$$

By combining the quinhydrone and hydrogen electrodes to form a cell, Bijlmann [20] found $e_0=0{\cdot}7042$ at 18° C., the former

electrode being positive. If $e_{cal.}$ is the potential of the calomel electrode in relation to the hydrogen electrode, the former being positive, the voltage (E') of a calomel-quinhydrone cell is

$$E' = e_0 - e_{cal.} - 0{\cdot}000198 \,.\, T \,.\, \text{pH},$$

or,

$$\text{pH} = (e_0 - E' - e_{cal.})/0{\cdot}000198 \,.\, T.$$

The pH of the solution may thus be found by combining the quinhydrone electrode, instead of the hydrogen electrode, with the calomel electrode. Table 4, p. 144, gives values of both e_0 and $e_{cal.}$ at different temperatures, the former being calculated from the expression $e_0 = 0{\cdot}7175 - 0{\cdot}00074t$, where t is the temperature in °C.

The quinhydrone electrode in a buffer solution has also been used as a standard or comparison electrode by Veibel,[1, 21] since it is more accurately and rapidly reproduced, though less permanent, than the calomel electrode. Two quinhydrone electrodes thus combined would be analogous to a hydrogen electrode-concentration cell, and $E' = 0{\cdot}000198 \,.\, T \,.\, (\text{pH} - \text{pH}')$. The quinhydrone electrode, in fact, behaves as a hydrogen electrode in which the pressure of hydrogen is of the order of 10^{-24} atmospheres. For this purpose a mixture of 100 c.c. of $0{\cdot}1N$ hydrochloric acid and 900 c.c. $0{\cdot}9M$ potassium chloride solution is suggested for use in the electrode, since the standard quinhydrone electrode so produced will then always be positive to solutions of pH greater than 2·03. Then:

$$\text{pH} = 2{\cdot}03 + E'/0{\cdot}000198 \,.\, T.$$

The Electrode.—The actual electrode is extremely simple, for it consists of a piece of clean, bright (*i.e.*, unplatinised) platinum or gold wire, gauze, or foil, 1 cm. square, attached to a glass tube as already described (p. 41), which passes through the stopper of a small bottle or other suitable vessel (*e.g.*, a calomel electrode vessel or a test-tube). Provision is also made for a connecting "bridge." The metal must be carefully cleaned in a hot solution of potassium dichromate in strong sulphuric acid, well-washed with distilled water and ignited in the flame of an alcohol lamp (do not use a coal gas flame).

In some cases (*e.g.*, with milk products) gold or gold-plated platinum has been found preferable to platinum as an electrode material. Clean platinum is easily plated with gold if it is made the cathode in a 1 per cent. solution of potassium auricyanide, with a gold anode, for 3 minutes at 6 volts, and a current-density of 0·2 amp./sq. cm.

To set up the electrode, about 15 c.c. of the solution are shaken with a pinch (about 50 mgrms.) of quinhydrone, so that there is a slight excess of solid, and after about a minute the final potential is attained. When there is any sign of a continuous change in the potential, the electrode should be cleaned.

Quinhydrone.—The quinhydrone is prepared [22] by the mild oxidation of hydroquinone by ferric ammonium alum. A solution of 100 grms. of the alum in 300 c.c. of water at 60° is added gradually to a solution of 25 grms. of hydroquinone in 100 c.c. of water at 65°, and the mixture stirred.

$$2C_6H_4(OH)_2+O=C_6H_4O_2,C_6H_4(OH)_2+H_2O.$$

The fine crystals of quinhydrone (15 grms.) which separate when the liquid is cooled in ice are filtered by suction, washed with 100 c.c. of ice-cold distilled water, recrystallised from water at 80°, and dried for two days at room temperature. It is important that both iron and acidity should be absent, though Bijlmann and Jensen [23] state that though different methods of preparation produce the same results, and though traces of impurities have negligible effects, it is advisable to shake the quinhydrone with the test solution, pour off the liquid, and add a further quantity of solution for the actual test.

Limitations of the Electrode [24].—If the pH is above 8, the hydroquinone will ionise and produce hydrogen ions, and the simple formula given above will not apply. Methods which overcome this difficulty are available, *e.g.*, Parker [25] states that the pH of well-buffered solutions can be measured up to pH 10 if the readings are taken rapidly. Modifications of the electrode also exist for the same purpose, but they are not widely used for routine work, and the electrode is not recommended in such cases. Similarly, any reaction which oxidises the hydroquinone or reduces the quinone, and so upsets the equimolecular proportions required for the formation of quinhydrone, will render the simple formula useless. Interfering oxidising or reducing agents may be tested for by the addition of quinone or hydroquinone to the solution until the potential is the same as that obtained when quinhydrone is used. If quinhydrone is then added and the potential remains unaltered, the electrode may be taken as accurate. Badly-buffered solutions, also, cannot be used unless readings are made very rapidly and the highest recorded value taken, since their pH is affected by that of the quinhydrone. The electrode is also subject to salt and protein errors, but these errors differ from those of the hydrogen electrode (p. 68), since the activities of the quinone and hydroquinone are altered to different extents. In $2M$ solutions the protein error may be of the order of 0·1 pH. The salt error is not large, and may be overcome by the use of the "hydroquinhydrone" electrode, in which the quinhydrone is replaced by a mixture of 1 grm. of hydroquinone and 0·1 grm. of quinhydrone, both in the standard and test solution, the metal electrode being immersed in the undissolved residue.[26] The correction is as small

as −0·02 pH for 0·5*M* salt solutions, but rises to −0·20 pH for 4*M* solutions. The limitations of electrodes in general are discussed on p. 67.

The quinhydrone electrode gives excellent results in solutions of strong acids, oxalic, acetic, malonic and citraconic acids, and of borates, phosphates (up to pH 7·7), alkaloids, etc. Since no gas phase is involved as in the case of the hydrogen electrode, it is particularly suited for biological work, *e.g.*, in presence of carbon dioxide (Cullen[26]) or of oxygen. It may be usefully employed to replace the hydrogen electrode in dilute solutions of nitric acid or of unsaturated organic acids. Weak or slowly-acting oxidising agents (*e.g.*, nitrates), also, will not appreciably affect it, though stronger reagents (*e.g.*, chromates, ferric chloride) interfere. O'Sullivan[27] has obtained satisfactory results with neutral and weakly acid solutions of copper, tin, lead, and nickel salts, but not in even moderately acid solutions of mercury, silver, or gold. The wide uses of this electrode in control of pH in industrial processes are indicated in Part IV.

The Glass Electrode and Other Electrodes

The Glass Electrode.—This electrode, the early work on which has been summarised by the writer,[28] is becoming more and more an instrument for the routine determination of pH values. This is due largely to the work of Kerridge,[29] who intended it principally for biological work. But since it is independent of salt and protein errors, and of substances which poison the hydrogen or quinhydrone electrodes, and since it may be used with coloured or turbid solutions or pastes of pH 1 to 13, it has found many practical uses (see p. 51). The cell, which is shown in Fig. 13, may be easily made after a little practice. A bulb A is blown on the end of two pieces of clean glass-tubing C and D in the ordinary way, and the thinnest portion of the surface slightly warmed and drawn in to form a depression B, the glass between B and A being about 0·03 mm. thick. A is filled with a buffer solution of known pH (about 7 or 8) by means of the tubes C and D, C is stoppered and the connecting tubes of two calomel electrodes placed in B and D. B holds the test solution (0·5 to 2 c.c.), the surface of which may be covered with a layer of medicinal paraffin to exclude air and electrical leaks. Cheap, soft soda glass is best for the purpose, and borosilicate, potash, or alumina glass or pyrex should not be used. Certain of these behave as sodium electrodes in some solutions. The electrode stands on an insulated glass plate E.

A more robust form, due to McInnes and Dole,[30] is prepared from a very thin glass bulb which has been blown out till inter-

ference colours are produced. A thin, flat portion is selected, and placed over the end of a piece of ordinary soft glass tubing heated to redness. The diaphragm should fuse on and produce a small and compact electrode.

Since the potentials of the calomel electrodes balance one another when the connections are made, the *E.M.F.* of the cell is obtained directly. The potential due to the glass and any inaccuracies in the calomel electrodes (E_1) is eliminated by taking a reading (E_2) with a $0{\cdot}05M$ potassium hydrogen phthalate solution (pH 3·97) in B, and then with the test solution (E_3), the same buffer of pHx being retained in A throughout. Since the potential-difference between A and B is proportional

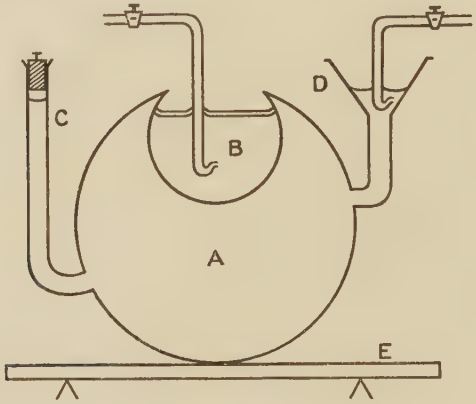

Fig. 13.

to the difference in the pH values of the solutions they contain, and if y is the pH of the test liquid, then :

$$E_2 = 0.000198 \,.\, T \,.\, (x - 3{\cdot}97) + E_1,$$

and $$E_3 = 0.000198 \,.\, T \,.\, (x - y) + E_1,$$

whence, $$y = 3{\cdot}97 + (E_2 - E_3)/0{\cdot}000198 \,.\, T.$$

The great disadvantage of the method is the technique and apparatus required. The high resistance of the glass membrane precludes the use of an ordinary galvanometer as a null-instrument (see p. 60), and elaborate precautions for insulation and shielding must be taken. A Dolezalek, Compton, or, preferably, a Lindemann electrometer is used, while Elder and Wright [31] and Partridge [32] recommend a vacuum tube potentiometer. The Lindemann type is most easily set up, and may be used for portable sets, and the best circuit is usually supplied with the

instrument. Under ideal conditions the error is of an order corresponding with 0·008 pH.

Other Electrodes.—Other electrodes are mainly of theoretical importance or have been devised for special purposes. They include oxygen, air, chlorine, and other gas or metal and metal oxide electrodes.[33] In certain cases an ordinary platinum wire is placed in the solution (see p. 110), while antimony electrodes [34] are sometimes used (*e.g.*, for soils, p. 103).

Summary.—The hydrogen electrode is the standard electrode, but is easily upset by "poisons," salts, proteins, etc. The quinhydrone electrode is less easily upset, but cannot be used in alkaline solutions or in the presence of oxidising or reducing agents. The glass electrode may be used in all solutions, but elaborate apparatus and technique are required. The hydrogen electrode is, therefore, usually employed, the quinhydrone electrode being useful in special cases. The glass electrode is used relatively little for the reasons mentioned.

Bridging Devices [35]

The use of potassium chloride solution for this purpose has already been discussed (p. 38). With reference to the apparatus,

Fig. 14A.

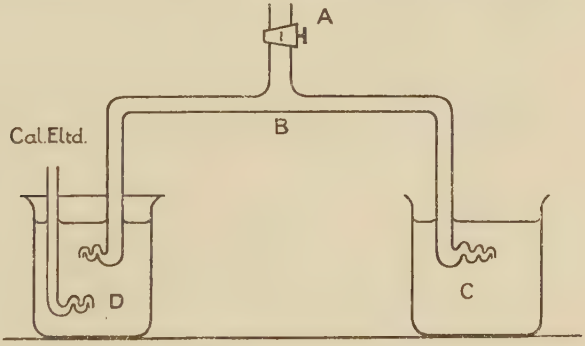

Fig. 14.

that shown in Fig. 14 has the merits of efficiency and simplicity. It consists of an inverted glass U-tube about 3 mm. in diameter, to the middle B of which is attached a branch tube closed by the tap A or by rubber tubing and a spring clip. The ends, which are drawn off to an aperture about 1 mm. wide, are bent as shown (Fig. 14A) to minimise diffusion. The tube is completely filled with a saturated solution of pure potassium chloride by means of a small funnel attached to the tubing, care being taken that no bubbles are included, and the ends are then dipped (C) in the

test solution containing the hydrogen (or other) electrode, and (D) in a small beaker of saturated potassium chloride solution, through a hole in the cover of which passes the connecting tube from the calomel electrode.

Care should be taken that the end C is as far as possible from the hydrogen bubbles, as a bubble of gas (or air) will break the electrical connection. Further, the levels of liquid in the electrode and potassium chloride vessels should be the same, or one will siphon into the other. This, however, may be avoided by the use of an ungreased three-way tap at B, instead of A, which may be completely closed without breaking the electrical circuit when readings are being taken so long as there is a thin film of solution round the inside of the barrel of the tap to act as an electrical connection.

The writer does not recommend wads of filter-paper, agar jellies, or layers of sand to stop diffusion from the ends of the connecting tube. They increase the resistance of the circuit and introduce another possible source of error, whereas the simple method described above is usually just as effective. In the unlikely event of a protected liquid junction being necessary the modification suggested by Waterman [36] is very convenient.

CHAPTER III

ELECTROMETRY, OR THE MEASUREMENT OF ELECTROMOTIVE FORCE

Principles Involved in Electrometry

In the ideal case, an ordinary voltmeter connected to the terminals of the hydrogen-calomel electrode cell would be the simplest and most direct means of measuring the voltage of the latter. Such instruments, however, require so much current that they cannot be used in this way, and the principle of balance or compensation is usually employed. Unfortunately this means that continuous and automatic readings cannot as a rule be made, though the valve method described on p. 56 is a first step in this direction. It has also been stated that the current of 5 micro-amps. obtainable from a benzo-quinhydrone-calomel cell may be measured directly and fairly accurately by the Cambridge automatic, recording, thread-voltmeter without appreciably disturbing the *E.M.F.* of the cell.

The Poggendorff Compensation Method.—This method is commonly employed in electrometry, and as in its simplest form it requires only the cheapest and most easily constructed apparatus, it will be described in detail. If every electrically conducting wire is imagined to be a pipe (a high resistance wire corresponding with a dipe of narrow bore and *vice versâ*), and every battery a pump whose force depends on its voltage, then for simplicity the flow of electricity may be compared with that of water in the following explanation. Imagine (Fig. 15), a cell (A) such as an accumulator giving a constant *E.M.F.* (about 2 volts), with each of its terminals attached to one end of a uniform length of resistance wire BC. If B is connected to the positive terminal there is a fall in potential between B and C, corresponding with the voltage of A, and therefore the fall in potential

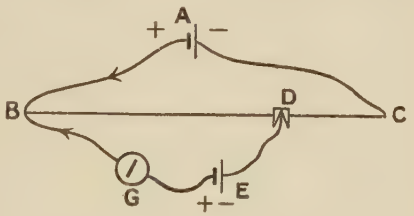

Fig. 15.

between B and any point (say D) on the wire will be proportional to the length of the wire (BD) between B and that point; that is, it will equal the fraction BD/BC of the total fall in potential along the wire.

If now the positive terminal of another cell E of *E.M.F.* less than that of A is also connected to B through a galvanometer (G), the wire connected to its negative terminal may be moved up and down BC until a point D is found where G indicates no current at all. The cell E then compensates the fall in potential of A between B and D, *i.e.*, E/A=BD/BC, and if A is known, E may be found from BD and BC.

In practice it is found more convenient to avoid the use as a standard of the accumulator A, the *E.M.F.* of which is not constant, and is not accurately known. An accurately standardised cell (E′) is accordingly substituted for E and a new reading taken. If the new point of zero current is D′, then E′/A=BD′/BC. If, further, the two readings are taken in rapid succession, the *E.M.F.* of A will be the same for both, and by division of the two ratios E . A/E′ . A=BD . BC/BD′. BC,

$$i.e., \quad E/E' = BD/BD'.$$

The length of the wire BC is also eliminated and E is the only unknown quantity.

Direct Measurement with a Voltmeter.—In the method usually employed a standard cell is not required, but a voltmeter is connected to one end of the measuring wire and to the point of balance. Valve methods (p. 56), however, also fall under this heading. The circuit suggested by Sand [37] is essentially that shown in Fig. 15, the voltmeter being connected to B and D. The zero-instrument is still required (Sand uses a compact form of capillary electrometer, see p. 61), but the measuring wire BDC need not be calibrated, and any adjustable resistance will suffice. A dry cell may be used at A, or a suitable resistance inserted between A and B so that the voltmeter is not unduly strained. The voltmeter should be graduated to read in millivolts from 0 to 1·5 volts, and should be accurately calibrated. Such an instrument is expensive, but where it is available this method is to be recommended.

It should be remembered that the terminals of a voltmeter are always connected directly to the two points between which the potential is to be measured, and that where the internal resistance of the cell is large, the voltmeter must be correspondingly delicate and require less current. A resistance of 150 ohms is suitable, or a large resistance in series with a galvanometer of the D'Arsonval type enables this form to be used to measure the *E.M.F.* of cells which give only very small currents. For example, an ammeter

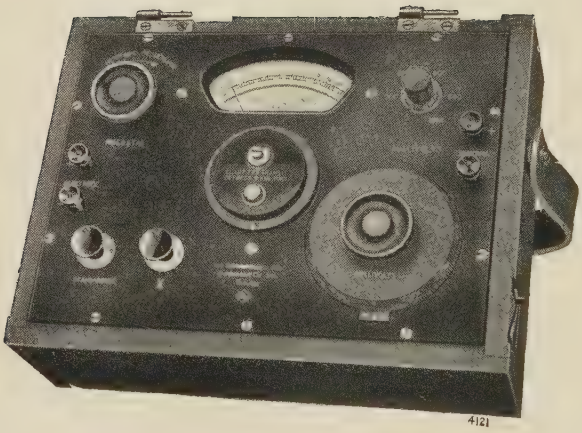

Fig. 17

PORTABLE POTENTIOMETER BOX

(Cambridge Instrument Company Ltd.)

reading in milliamps. with a suitable resistance, calibrated by means of a sliding wire resistance in series, makes an excellent millivoltmeter. Fig. 16 shows a circuit in which the fixed resistance R_1 and the variable resistance R_2 have only to be adjusted so as to make full

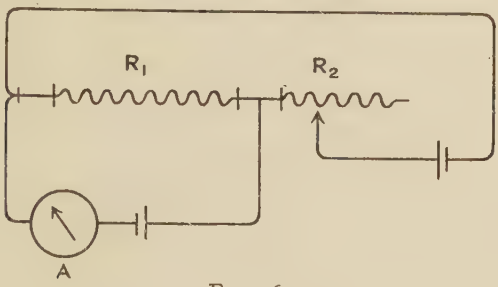

Fig. 16.

use of the scale of the milliammeter A. A balance may then be obtained and A calibrated in millivolts.

Of the many reliable made-up instruments on the market the principle of one only will be described, as the others do not as a rule differ greatly, and the writer has found this particular instrument robust, compact, and reliable to 1 millivolt. It is

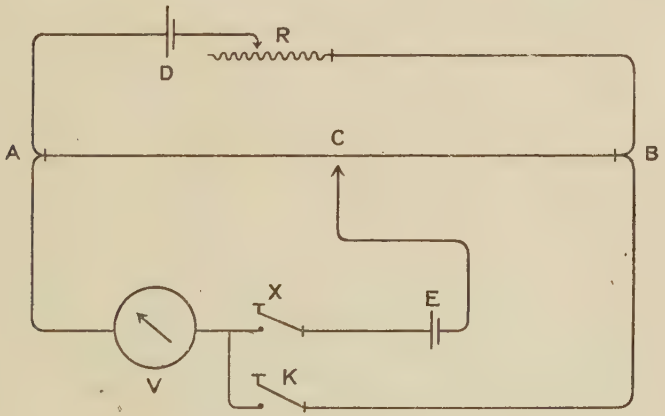

Fig. 18.

shown pictorially and in simple circuit form in Figs. 17 and 18, and is made by the Cambridge Instrument Co. The tapping key K is depressed, and the coarse resistance R adjusted till the voltmeter V shows a reading of 1 volt, D being an ordinary

single dry cell connected to the terminals on the left. The fall in potential along AB is then 1 volt. The cell to be measured (E) is then connected to the terminals on the right, the key X depressed lightly, and the point C found such that the voltmeter records zero. Then, if AB is calibrated in 1000 parts, each part is equivalent to 1 millivolt, and the distance AC gives the voltage of E. Actually, in the Cambridge instrument the wire AB is replaced by a coil tapped at five 200-millivolt intervals, and a circular slide wire (90 ohms) for fine adjustments graduated from 0 to 200 millivolts. To use the voltmeter directly, for small voltages, the dials are set to zero (*i.e.*, C is moved to A), and X depressed. This method, however, is not advisable for pH work, and in any case should only be used for the measurement of very small voltages on account of the strain on the delicate unipivot galvanometer which is the indicating instrument of the apparatus.

The Thermionic Valve Method.—This method will be described shortly because, in the author's opinion, it is the method of the future and admits of great possibilities for the automatic determination and recording of pH values. Moreover, with the popularisation of wireless, valves have become commercial articles, and every one is familiar with their action.

As already explained (p. 53), a voltmeter cannot be used directly to measure the voltage of an electrolytic cell because it consumes too much current. If, however, a galvanometer is converted by means of a thermionic valve from a null-point to a direct-reading instrument a great advantage is obtained in that the reading is continuous, and by means of suitable mechanism may then be made to function automatically, and even to record the readings.

Goode [38] selected a valve requiring 20–100 volts between the plate and filament. The current C through the plate circuit may be then considered to be made up of two constituents, viz. C′ a current independent of the grid potential, and (C–C′) which is almost a linear function of the grid potential. If C′ is balanced by means of an equal current in the reverse direction, the remainder (C–C′) may be measured with a galvanometer or micro-ammeter, calibrated, if required, directly in pH values. No current, therefore, is taken from the cell, the potential of which is indicated continuously by (C–C′). In a few words, the steady plate-current is balanced out, so that only voltage variations on the grid are measured.

The circuit is shown in Fig. 19, the electrolytic cell C being connected to the grid of the valve V and the negative pole of the 6-volt battery B. The high-tension battery T supplies 20–100 volts to the plate of the valve, and the adjustable 1300-ohm resistance (R_1) serves to steady the current. R_2 is a 25-ohm

resistance shunted across the D'Arsonval mirror galvanometer G, while the 0·6 ohm resistance R_3 maintains a steady filament current.

This is the circuit in its simplest form. By the use of amplifying valves, however (see Goode, *loc. cit.*), the current may be magnified (*e.g.*, 25 times) and measured directly and continuously by means of a milliammeter calibrated in pH values.

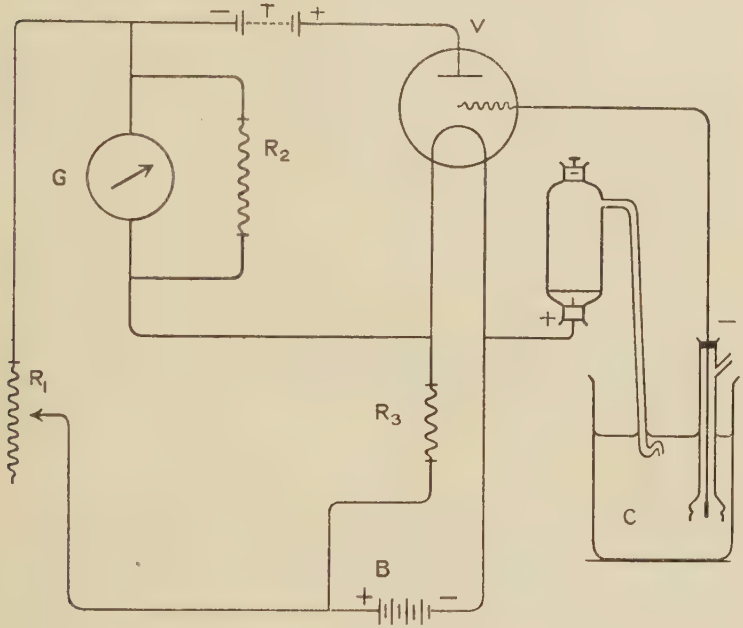

Fig. 19.

This may be used as a voltmeter by adding a suitable resistance, and, further, it may be used for recording purposes.

Such methods [39] are excellent for high-resistance cells (*e.g.*, glass electrodes) and for electro-titrations. A maximum accuracy of 0·02 pH is obtainable, and if the characteristics of the valves remain constant they do not require to be calibrated.

Electrometric Equipment

The Working Cell.—As mentioned above, an accumulator is most suitable for the purpose as the current is usually fairly constant. Two or three cupron cells in series (*E.M.F.* 0·85 volt

each) may be used, however, where there are no charging facilities. The care of accumulators is generally well understood nowadays, but a few practical hints are appended.

Use sulphuric acid of the necessary density (1·18 to 1·25), and charge and discharge at the rates suggested by the makers. Charge weekly, whether the cells have been used or not, and allow them to gas freely for a while before the charge is stopped. Add distilled water as the liquid evaporates, so that the level is 1 cm. above the plates. Recharge before the voltage falls below 2 volts, and keep the plates and leads well insulated and vaselined to avoid electrical leaks. An adjustable sliding resistance switch should be inserted between the cell and one of the terminals of the measuring wire as shown in the diagram of the complete apparatus (Fig. 23, p. 63), so that the cell is discharging only when readings are being taken. Since *E.M.F.'s* less than 2 volts are to be measured, one cell will suffice, but it should have a fairly large capacity (40–60 ampère-hours), or it will run down rapidly.

The Measuring Bridge, Rheostat, or Potentiometer.—This may be constructed by tightly stretching a length of resistance

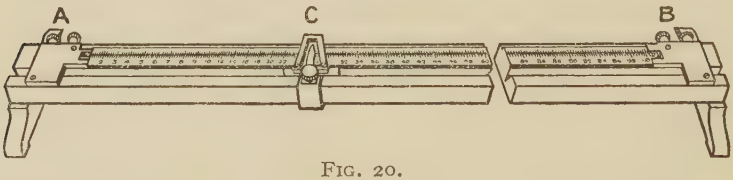

Fig. 20.

wire against a metre scale screwed on an oak base-board (Fig. 20). The points A and B on the wire, corresponding with 0 and 1 m. on the scale, are soldered to copper strips which are, in turn, fixed to binding screws attached to the board. The sliding contact C is a metal jockey free to move in a groove in the board, and provided with a pointer and a piece of metal to which is attached an insulated knob, and on the underside, a small piece of platinum wire. The latter is arranged at right angles to the direction of the measuring wire and makes contact with it only when the knob is depressed. A binding screw serves to connect up the jockey with the rest of the circuit.

The choice of alloy for the wire is determined by (*a*) resistance to damage by the pressure of the sliding contact; (*b*) resistance to tarnish; (*c*) absence of thermoelectric effect when in contact with copper; (*d*) suitable resistance per unit length, *e.g.*, the wire must not heat up, nor should it carry too much current. Manganin, gilded to prevent tarnishing, satisfies most of these conditions, otherwise eureka (No. 20 or 34-gauge), constantan, or platinum-iridium may be used.

Since the fall in potential along 1 metre (1000 mm.) of wire is 2 volts, each mm. will correspond with 0·002 volt (*i.e.*, 2 millivolts). If the wire is uniform it should be possible to measure accurately to 0·5 mm. and thus obtain an accuracy of 1 millivolt, which is ample for most purposes.* Indeed, the accuracy of the method is limited by the sensitiveness of the galvanometer rather than by the bridge. If, however, it is considered necessary, the wire may be calibrated by the method of Strouhal and Barus.[40] Alternatively the measuring wire may be replaced by two tapped coils in series, one calibrated to correspond with intervals of 0·1 volt, whilst the other serves as a fine adjustment for voltages down to 1 millivolt. Ordinary two-decade post office resistance-boxes may also be used for this purpose.[41] Direct reading instruments are described below (p. 71) and are easily constructed.

The Standard Cell.—The cadmium or Weston cell, which is easily reproduced and little affected by temperature changes, is usually employed as standard.

The H-shaped vessel used for the purpose[9] (Fig. 21) is easily obtainable, and is mounted in a box on a large cork cut to shape, the platinum electrodes (which may be amalgamated with mercury) being connected to insulated terminals. Warm 2 grms. of pure zinc-free cadmium with 14 grms. of purified mercury (see p. 40) in a test-tube on the water-bath, stir well, and pour enough of the amalgam into one limb of the H-vessel (immersed in hot water) to cover the platinum to a depth of 0·5 cm. The amalgam (4) solidifies on cooling. Prepare also a saturated solution of pure cadmium sulphate ($CdSO_4,8/3H_2O$) below 75°, by grinding the salt with water in a mortar. Pour off the liquor, and place a thin layer (5) of the residual powdered crystals, 1 mm. deep, over the amalgam.

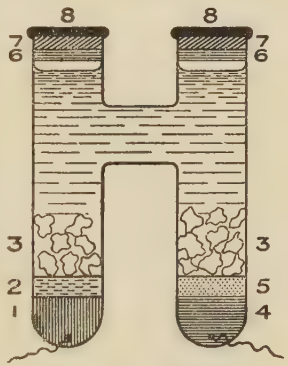

FIG. 21.

The platinum in the other limb is covered with a layer 1 cm. deep of pure mercury (1), over which is spread 3 mm. of mercurous sulphate paste (2) prepared by grinding mercurous sulphate, cadmium sulphate, and its saturated solution in a

* If the resistance C in Fig. 23 (p. 63) is adjusted so that the Weston standard cell (*E.M.F.* 1018 millivolts) is exactly balanced for a bridge-wire reading of 1018 millimetres, then the *E.M.F.* in millivolts of the unknown cell will be given without further calculation by the reading in millimetres on the bridge-wire, if this setting is maintained and the point of balance found with the unknown cell in circuit.

mortar to form a thin cream. Mercuric sulphate may be removed by filtering the liquid through cotton wool by means of a pump, and rubbing up the residual paste with more solution. One further repetition of this process suffices. Layers of large crystals of cadmium sulphate (3) are added, and the vessel filled with saturated cadmium sulphate solution and closed with a layer of paraffin (6), a disc of cork (7), and finally with sealing-wax (8). An air bubble, to allow for expansion in hot weather, may be introduced by piercing the wax layer with a pin, and closing up the hole again by means of wax with the vessel in an inclined position.

Such a cell has an *E.M.F.* of 1·0189 volts (5–10°), which falls by 0·1 millivolt at 15°, and by a further 0·2 millivolt each at 20° and 25° (1·0184 volts at 25°). It should not be used for twenty-four hours after it has been prepared, and should be checked, if possible, against another such cell of known or certified voltage. The mercury terminal is positive.

The Electrical Zero Instrument.—In the Poggendorff method an electrical instrument is required only to indicate, by absence of motion, when no current is flowing through the circuit, and the question of sensitiveness as distinct from accuracy is therefore all-important. Such instruments fall into two classes:

(*a*) *Galvanometers.*—A galvanometer is an instrument in which a current flowing through a coil suspended in the magnetic field of a strong magnet causes it (the coil) to turn to an extent depending on the current, and to turn with it a needle or other indicating device. It is a most sensitive and convenient instrument, but its use is limited if the resistance of the cell measured is very high, and also by the fact that it is very sensitive to shock or vibration. A good instrument of fairly high resistance should indicate 10^{-9} amp. corresponding with an *E.M.F.* of 1 millivolt or less. A resistance wire suitably connected in shunt across the terminals of a galvanometer takes some of the current and induces a field of force which opposes to some extent the motion of the coil, and thus "damps" the swing so that the pointer comes to rest without undue oscillation.

The British Scientific Instruments Research Association has recently issued a guide [42] to the choice of electrical instruments. It is pointed out that the damping effect is often too small, *i.e.*, too violent a swing of the needle is produced when the instrument is first switched into the circuit. Damping should be almost but not quite critical, so that the needle swings slightly beyond, and then returns to its final position. Other points to be noted are change of zero during use, and the effect of temperature. Clark [24] recommends an instrument with a coil resistance of 510 ohms, critical damping resistance 10,000 ohms, period 5·4 secs., sensitiveness (*i.e.*,

resistance required in the circuit to give a deflection of 1 mm. when 1 volt is applied) 1973×10^6 ohms.

(*b*) *Electrometers.*—These, as a rule, are less sensitive than galvanometers, but since for small *E.M.F.'s* they behave as static instruments, they are not affected by the resistance of the cell. They themselves have a high resistance, and are "dead beat," *i.e.*, they reach their final position without oscillation. A useful and easily obtainable type is the capillary electrometer shown in Fig. 22. It consists essentially of two glass tubes A and B about 0·5 cm. in diameter, and joined by the capillary tube C. One (B) has a bulb blown on the end, and both are provided with platinum electrodes joined to screw terminals (*a* and *b*), fused through the glass or inserted through tubes in the manner already described (p. 41). Pure mercury (p. 40) is poured into the tube A till the level is about halfway up the vertical portion of the capillary tube. The bulb in B is half-filled with mercury, and the remainder of B filled with dilute sulphuric acid (1 vol. in 8), which has previously been well-boiled, cooled, and shaken with a little pure mercury. The acid is drawn into C by gentle pressure applied on A, which forces a few drops of mercury into B; when the pressure is released, the acid follows the mercury surface back into C, though it must not enter A. The open ends of A and C are lightly stoppered or sealed.

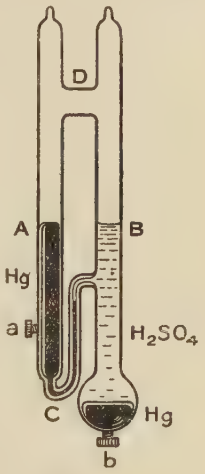

FIG. 22.

The principle of the instrument is as follows (Lippmann, 1873). The surface tension of the surface between the mercury and the acid is decreased if the mercury is positively charged, and *vice versâ*. When the tension decreases expansion of the surface occurs, and if the surface is in a vertical tube it will rise. Conversely, it will fall when the mercury is negatively charged, because the increase in surface tension causes contraction. If the charges are exactly neutralised there is no motion. Consequently a potential difference applied between A and B moves the surface up or down to an extent which, for small potentials, is proportional to the *E.M.F.*

There are a few important precautions to be observed. Firstly, the positive current from the cell being measured should always travel from B to A, *i.e.*, B should be connected to the positive terminal and A to the measuring wire. This is to prevent the formation of mercurous sulphate in the capillary tube should an unduly large current be accidentally applied, and

in this connection it is important to note that the least trace of dirt in the capillary will interfere with the movement of the surface. As soon as this shows the least sign that it is sticking, the electrometer should be emptied and cleaned by treatment in succession with hot nitric acid, a hot solution of potassium dichromate in concentrated sulphuric acid, and a plentiful supply of distilled water, and finally dried by a stream of warm air filtered through cotton wool.

With the connections made as described there is little danger of fouling the capillary, though an excessive current may produce a minute bubble of hydrogen by electrolysis. This is easily removed, however, by forcing a drop of mercury over into B, and thus providing a clean mercury surface.

Many of the instruments sold are exhausted of air, and the ends of A and B hermetically sealed, these two tubes being connected by a cross-tube D above the mercury surfaces. A clean mercury surface is then easily obtained by tipping the electrometer so that a few drops of mercury fall into B. These instruments are excellent until they become fouled through constant use, and they must then be opened up and cleaned in the usual way. For obvious reasons currents should not be passed through the electrometer for longer than can be avoided. It is best to use an ordinary double-contact Morse tapping-key to complete the circuit, and to arrange the connections so that when the key is released the electrometer is short-circuited and the meniscus enabled to return to its zero position (see H in Fig. 23). The sensitiveness is sometimes increased by a very small negative polarisation applied before the reading is taken. The capillary tube also should be wetted before use by gentle suction and gentle pressure applied at A so that the level moves up and down a few times.

The movements of the meniscus are very small near the zero-point, and are best observed through a microscope or lens, the electrometer being clamped in a suitable position with a small mirror behind and just above the capillary tube, to reflect light on to the mercury surface. A small slip of glass cemented on the outside of the tube with Canada-balsam sharpens the image of the meniscus, or the tube itself may be lens-shaped. A scale in the microscope assists the measurement of the distance travelled by the meniscus and under ideal conditions a voltage of 0·1 millivolt may be indicated, though 1 millivolt is the usual degree of accuracy. The procedure for the actual measurement is described on p. 65.

Some space has been devoted to the capillary electrometer because it is cheap, convenient, easily constructed, and if not mis-used will give excellent results. Other types of electrometer

(*e.g.*, the Dolezalek quadrant electrometer) may be used, but they are troublesome to adjust, and the capillary type may be confidently recommended even where these are available.

Wiring, Insulation, etc.—Fig. 23 shows a diagram of the complete circuit suggested for this method in which A is the working cell (accumulator) controlled by the plug-in switch B and the coarse back-resistance C, DE is the measuring wire, F the slider, G the capillary electrometer which may be thrown into circuit or short-circuited according as the Morse tapping-key H is down or up respectively. The double-pole switch J enables either the cadmium cell K, or the calomel-hydrogen electrode cell L containing the test solution, to be measured. A two-way switch may readily be made from three cups of mercury,

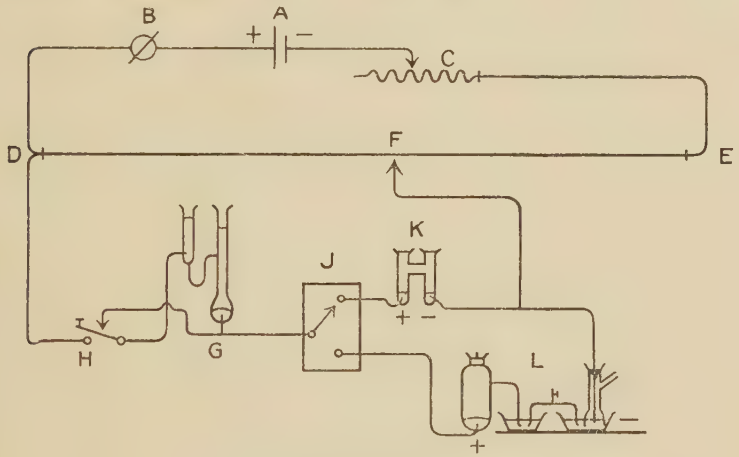

Fig. 23.

scooped in a block of paraffin wax, any two of which may be connected by a piece of thick copper wire in a glass tube with bent amalgamated ends dipping in the cups.

Well-insulated copper wire, the ends of which are scraped bright, should be used for connections. Unnecessarily long connections should be avoided. Permanent connections such as those from the platinum wires of an electrode or capillary electrometer should be soldered, but stout binding screws are preferable for all other purposes as they are easily disconnected. Platinum-tipped copper wires are advisable, but not essential, for connections made in mercury, as copper alone has been said to cause the mercury to siphon out. Knife-edge or plug-in switches should be used, and tapping contacts should be tipped

with platinum. The apparatus should be cleaned, and the connections scraped bright and tightened periodically. It is advisable to insulate all points of connection, and it should be remembered that electrical leakage may occur across dirty or moist surfaces even if these are normally non-conductors.

Under certain circumstances currents are picked up by the measuring apparatus. These may be the result of the production of a potential difference between two points owing, for example, to the potential between the electric lighting mains and earth. If this is suspected the whole apparatus should be brought to the same potential by mounting it on a large sheet of metal, which is itself connected to earth by means of a wire soldered to a water tap.

CHAPTER IV

TECHNIQUE—SOURCES OF ERROR—CALCULATION OF RESULTS

It cannot be pretended that no technique is required for the determination of pH values by this method. It is only by experience, in which the observer learns to "know" his apparatus, that really reliable results are obtained. At the same time this technique is rapidly acquired, and there is not the slightest reason why a worker with no specialised knowledge of electrochemistry should not soon learn to recognise if his readings are trustworthy, and if not, why not. The following pages, in which every common source of error is dealt with, are intended as a guide to this end. Notes referring in particular to the quinhydrone electrode are given on p. 48.

Making a Measurement.—(1) See that all electrical connections are tightly made, that the electrode vessels are clean and properly filled, and that there are no air bubbles in the narrow tubes carrying connecting-liquids. This applies especially to the "bridge." The outlet of the calomel electrode should be flushed out with potassium chloride solution, and the galvanometer, capillary electrometer, or other zero or indicating instruments should be adjusted and in good working order. The cell used as a source of potential (accumulator or dry battery) should be connected to the measuring wire shortly before the experiment begins, as the voltage often falls off slightly to a constant value during the first five minutes on an open circuit.

(2) Place the test-solution in the electrode vessel with precautions suitable to its nature. Shake with a little quinhydrone, or if the hydrogen electrode is used, bubble the purified gas at the rate of about two bubbles per second, and adjust the height of the electrode so that the liquid level rises and falls alternately between its lowest and mid-point.

(3) After about five minutes (or less in the case of the quinhydrone electrode) complete the liquid connections between the two half-cells. The whole apparatus should now have assumed the same temperature (*i.e.*, that of the room or thermostat), and this is noted.

(4) If the pH of the liquid is known approximately, adjust

the measuring instrument so that the reading corresponds with the value expected. If not, set the instrument to about the middle of the scale. Depress the key or contact lightly and momentarily, and note whether the galvanometer or electrometer makes a violent or gentle movement, and in which direction. Alter the instrument so as to oppose this reading, the correct direction having previously been ascertained by preliminary experiments. Endeavour in the same way to find two points as close together as possible for which small movements of the electrometer in opposite directions are obtained.

(5) From the above trials it should now be easy to find a point such that when the contact key is gently but firmly depressed for, say, three seconds, and then released, the instruments show no movement. This is the zero-point and gives the reading. If the sensitiveness is so great that some movement is always obtained, take the mean of two readings giving the smallest possible equal and opposite deflections.

(6) Remove the potassium chloride tube from the test solution, flush it out, and after two minutes replace it and take the reading again to see if there is any change. Repeat at one-minute intervals until three successive readings give the same value.

(7) Remove the potassium chloride tube from the test solution and flush it out.

(8) If a Weston or other standard cell is being used for comparison purposes, switch it into the circuit and find the new point of balance in the way indicated in (5).

(9) After the measurement has been made, remove traces of test solution from the potassium chloride tubes, wash the hydrogen (or other) electrode thoroughly with distilled water, and store it in a tube of distilled water (p. 45). See that the capillary electrometer is always left short-circuited, and that the supply battery is disconnected from the measuring wire. The needles of galvanometers, voltmeters, etc., should not be left in suspension. Finally, the electrode vessel should be cleaned and dried.

It is important to note (1) that there are no gas bubbles in the connecting liquids ; (2) that the potassium chloride tube is not in contact with the test-solution long enough to contaminate it or to become contaminated, and that the junction so formed is always fresh and not spoilt by diffusion ; (3) that no undue strain is placed on the galvanometer or electrometer by too violent a movement.

Standardisation of the Apparatus.—Initially, periodically, and before an important series of determinations, the apparatus should be standardised. The obvious way to do this is to use a buffer solution of known pH value, and although this provides

a check only over a small portion of the pH-range, it is usually sufficient, especially if the buffer chosen has a pH value not far removed from 7. When it is desired to read only to 0·1 pH the buffer need not even be prepared accurately so long as its pH value is subsequently determined with the desired degree of accuracy by the colorimetric method. The writer has even used tap-water in certain cases, while for low pH values 0·1*N* hydrochloric acid [35] is suitable, especially if the junction potential is eliminated by a 0·02*N* solution of hydrochloric acid placed between the 0·1*N* acid and the saturated potassium chloride solution.

A 0·05*M* solution of pure potassium hydrogen phthalate (10·209 grms. $KHC_8H_4O_4$ per litre), which has a pH of 3·97 and gives an *E.M.F.* of 0·480 volt against the saturated calomel electrode between the temperatures 20° and 30° C., is perhaps the most widely used standard. It is easily obtained pure and easily prepared, but unfortunately its solutions change in pH on storage (see p. 22). A more stringent test, which eliminates the somewhat unlikely possibility of the compensation of opposite errors in the electrodes, is to plot a titration curve (see p. 108), and to compare it with that obtained with an apparatus of known reliability.

Factors which may Influence the Electrometric Method

Temperature.—It is important that the temperatures of the three portions of the electrolytic cell should be the same as one another, and should not alter throughout the experiment. If the nature of the sample precludes this, a thermometer must be inserted in the electrode vessel, and the necessary correction applied. This may often be determined by a parallel determination with a solution of known pH value. The potentials of various electrodes do not vary with temperature to the same extent, as is shown in the temperature tables on p. 144. The temperature should always be noted for the purpose of calculating the results, but except in highly accurate work a latitude of a few °C. is permissible and will not affect the pH. For solutions at 40° or higher the calomel electrode is not suitable, as it has a time-lag. The quinhydrone electrode, however, may be used as a standard in such cases, and the *E.M.F.* of a hydrogen-quinhydrone electrode combination decreases by 0·76 millivolt for every rise of 1° C. between 0 and 60° C. Water-jacketed electrodes to ensure constant temperature have been designed by Simms.[43]

Poisoned Electrodes.—These are a common source of trouble, especially with the hydrogen, and to a less extent with the

quinhydrone electrode. Glass electrodes are almost immune. Fortunately poisoning is easily detected, and is denoted by a characteristic " drift " or uncertain " swaying " motion of the indicator of the galvanometer or of the mercury surface of the capillary electrometer, especially near the point of balance. This is readily distinguished from the firm and steady movement produced with a good electrode, and indicates that the platinum black is no longer playing its part as a catalyst of the equilibrium between ionic and atomic or molecular hydrogen. Sometimes matters will right themselves if the flow of hydrogen is stopped and the reading taken immediately, but as a rule the only course is to strip the electrode completely, to replatinise it as described on p. 45, and to restandardise the apparatus.

Hydrogen electrodes are apt to be fickle. Sometimes they will last for months and survive immersion in a variety of doubtful liquids. Others may fail for no apparent reason soon after they have been prepared. Usually a poisoned electrode gives a potential with too positive a value. Probably the method of preparation affects their subsequent behaviour, but that described on p. 45 has been found to give good results, and in this respect also a wire is not so easily poisoned as a plate electrode. Among the poisons for the hydrogen electrode are certain alkaloids, amino compounds, and proteins, toluene, ammonia, sulphides, cyanides, arsenic and mercury compounds, and to a less extent sulphur dioxide, hydrogen sulphide, and oxygen. In particular circumstances, however, certain of these (*e.g.*, mercury, ammonia, amines) may have no ill-effects, so that few general rules can be stated.

Sometimes the electrode is only temporarily disabled, and this is probably due to certain constituents of the electrolyte which though they produce disturbing effects, can hardly be classed as poisons (*vide infra*). Oxygen,[44] nitrogen, and other inert diluents of the hydrogen are examples. In this connection it may be mentioned that hydrogen electrodes may also be put out of action by floating or colloidal particles such as are found in suspensions of soils, flour, etc. These may be deposited on the platinum black and clog it, or they may damage it by abrasion, and in such cases the quinhydrone electrode will probably prove more suitable. Alternatively, a longer wire than usual may be taken for the electrode and lowered into the solution as required to replace the portion affected. The limitations of the quinhydrone electrode in this and other respects are discussed on p. 48.

The Protein Error.—This source of error is more fully discussed in connection with the colorimetric method (p. 98), but is not a serious factor in electrometric work, which may,

therefore, be used to standardise the colorimetric method. When the proteins are present in the colloidal state, however, they may give rise to the source of error mentioned in the preceding paragraph. Except where the concentration of protein is relatively high the error introduced is not large, but as proteins occur in many liquids of biological importance, their influence cannot be overlooked. Where the nature and approximate amount of the protein are known the error may be determined from the change in pH of a buffer of a certain pH value on addition of the same protein in the amounts concerned. The data given on p. 48 in connection with the quinhydrone electrode may be useful as a guide to the approximate magnitude of the error. In cases of extreme importance a check may be provided by the use of the colorimetric method, suitably corrected if necessary, or of another electrode (*e.g.*, a glass electrode).

The Salt Error.—Here, again, reference may be made to the colorimetric method (p. 97), though for the electrometric method the error is usually very small. High concentrations of salt may produce an error, probably on account of the change in hydrogen ion "activity," as distinct from its concentration (cf. p. 18). Even the glass electrode has been found (Hill [30]) to have a small salt error in the presence of ammonium chloride buffers of pH $>$ 8·6.

Oxidising and Reducing Agents [45].—Causes of failures have at various times, though not necessarily always, been experienced in the presence of oxidising compounds such as ferric salts, nitrates, chlorates and permanganates, or easily reducible salts such as those of lead, cadmium, and thallium. For the latter type of substance platinum foil is said to be preferable to wire, as the hydrogen is not so easily discharged. Strong reducing agents (*e.g.*, sulphur dioxide) may also produce anomalous results quite apart from their poisoning effects. In many cases check experiments with other electrodes or with solutions of known pH may be used. It will, of course, be understood that solutions containing metal ions electropositive to hydrogen will deposit these ions on the hydrogen electrode, and so limit its use. In such cases the quinhydrone electrode may replace it (see p. 49).

Badly Buffered Solutions—Adsorption.—These solutions are a source of error inasmuch as their pH alters while the reading is being taken, although the value actually obtained is correct at that moment. Certain solutions will absorb carbon dioxide from the air and so increase in acidity, and in such cases two electrodes may give different results. Others, however, may lose some of their dissolved carbon dioxide owing to the bubbling of the hydrogen, and though Evans [46] has stated that formic acid may be produced by the catalytic effect of the platinum on

the mixture of water, hydrogen and carbon dioxide, this explanation probably applies only to exceptional cases. The effect of changes in concentration of carbon dioxide is very important when liquids such as blood, beer, or natural waters are under investigation, and the methods or precautions employed are discussed in Part IV under the appropriate headings.

In general, the liquid may be placed in an air-tight electrode vessel with a quinhydrone electrode or hydrogen electrode of the non-bubbling type, or carbon dioxide may be fed in with the hydrogen at such a rate as to keep the concentration of gas in the liquid constant. In the case of beer comparable results are obtained after tossing the sample several times between two beakers to remove the excess of gas. In all such cases the determination should be made as rapidly as possible.

The effect of prolonged contact of buffers with glass containers has already been mentioned (p. 22), and the pH of badly buffered solutions is even more rapidly affected. Joseph [47] states that even a 0·0002*N* solution of hydrochloric acid has its hydrogen ion concentration reduced to about half in contact with glass for a short time, while silica suspensions and gels act even more rapidly. These phenomena, however, are better classified under the heading of *adsorption* of H ions by the solid matter, and it should be noted that in certain cases (*e.g.*, soils, p. 104) filtration may produce a change in pH value for the same reason.

Errors due to Electrical Equipment.—These are numerous, but will present no difficulty to the careful worker who will always take care that the electrical connections are well made, and that those parts which should be insulated or protected from electrical leaks are really so protected. Cleanliness cannot be insisted upon too strongly, and this applies especially to the platinum contact of the tapping-key and to the measuring wire.

Batteries that have run down may be a source of inconstant results, and bubbles in tubes making liquid connections may prevent any current whatever from flowing. An electrode (particularly the quinhydrone type) immersed in a liquid which is rapidly subjected to a large change in pH value (*e.g.*, in electrometric titrations) may become sluggish, and a capillary electrometer will suffer in a similar way if it is abused.

Miscellaneous.—It is not possible to do more than be prepared for the unknown, and there must be numerous cases of substances, other than those mentioned above, which, for no apparent reason, affect the electrometric method. Attention may be drawn, however, to the catalytic effect of certain substances as well as to that of the platinum black (p. 69). Bijlmann and Katagiri [26] record that dextrose affects both the hydrogen and quinhydrone electrodes. Alcohol and other solvents mixed with water in large proportions

reduce the ionisation of the electrolytes and consequently alter the pH value[54].

Useful notes on errors in general applied to physical chemistry are given by Findlay,[9] and the limitations imposed by the assumption of the theory of electrolytic dissociation have already been discussed (p. 18).

Summary.—From what has been written it may be imagined that the electrometric method is so limited in its safe application as to be almost useless. This is by no means so. The impression it is hoped to convey is that each case must be judged on its own merits, and that no general rule can be formulated. The fact that the hydrogen electrode is probably the most susceptible electrode and yet is certainly used more than any other is sufficient indication of its usefulness. At the same time cases are bound to occur when the results are suspect, and it is hoped that the above summary of possible, though not necessarily probable, sources of error may put the observer on his guard.

Calculation of Results

The simple formula (5) given on p. 37, viz.:

$$\text{pH}=(E-e_{\text{cal.}})/0{\cdot}000198\,.\,T,$$

where T is the absolute temperature, E the observed voltage, and $e_{\text{cal.}}$ the potential of the calomel electrode used, obviously provides the direct means of calculating results. As, however, this may prove laborious when a large number of determinations are being made with different calomel electrodes and at different temperatures, it is convenient to employ some means of eliminating calculations. This is particularly the case when it is required to find the *E.M.F.* which will be produced by the use of a solution (*e.g.*, a buffer) having a particular pH value. The translation of pH values into hydrogen ion concentration has already been dealt with (p. 14).

Several methods are available and fall into the following categories.

Electrometric Instruments reading directly in pH Units.—Where a direct-reading voltmeter, as opposed to a zero-instrument, is used, the voltage scale may be calibrated directly in pH values by means of the above formula. Thus, a piece of paper may be pasted over the glass protection-cover of the dial, or a table showing corresponding values of E and pH value may be kept at hand. Unless, however, several such scales are constructed this method will serve only when experiments are carried out with a particular calomel electrode, and at a particular temperature. As a matter of fact it is not usual to use more

than one type of calomel electrode, and as, moreover, the effect of small changes in temperature is not very great, this method will suffice for work where a high order of accuracy is not required.

Potentiometric Instruments reading directly in pH Units.—Where a zero-instrument is used with a potentiometer bridge, the latter may be calibrated directly in pH values in the manner already described, and the same considerations also apply. The worker will do well to test his calibrations in the first instance on a series of, say, five buffer solutions covering the whole pH and temperature ranges, and he will then be able to judge whether the desired degree of accuracy is obtainable on the scale chosen. If the apparatus and fall in potential along the wire are chosen as directed on p. 59, it is simply a matter of translating centimetres into pH values.

In Cole's modification of the Cambridge portable instrument (p. 55) a standard cell is introduced and the scale is calibrated so as to give directly the algebraic difference between the pH value of the test solution and that of a known buffer solution. The current from a 2-volt battery is adjusted to give a drop of 200 millivolts or 4 pH units per 90 ohms, and since ranges of 1200 millivolts (*i.e.*, 24 pH units) are provided, any temperature or arrangement of electrodes may be used.

Other ingenious plans have also been suggested. Thus, Behrens[48] uses a scale with two sliding contacts, one of which is wired to the electrometer, whilst the other forms one of the connections to the working cell, the other connection of which is fixed to one end of the measuring wire in the usual way. The first contact is moved to the potential of the standard cell and the second is then moved till the electrometer shows no motion. The scale is calibrated in both millivolts and hydrogen ion concentrations. This method takes no account of temperature. Hock's method[49] provides for all temperatures and electrodes, but is difficult to construct. It consists of a circular metal sheet with inner and outer scales (millivolts and pH values) with a spiral scale for temperature corrections.

Nomograms.—The writer has therefore designed a hydrogen ion nomogram which is cheaply and easily constructed, and which provides a rapid means for the translation of millivolts into pH values or the reverse. It is shown in Fig. 24 on p. 152, and is used as follows. (1) The edge of a thin, stiff piece of cardboard is marked off as shown in the small diagram labelled "indicator," and the three points labelled *C*, *D*, and *E* to represent the saturated 1·0*N* and 0·1*N* calomel electrodes respectively. (2) The reading in millivolts is then found on the line *AB*, the top scale being used for the quinhydrone electrode, and the bottom scale for the hydrogen electrode. (3) The vertical line on the electrode-indicator corresponding with the particular calomel electrode used is then placed at the millivolt reading on *AB* and

the position of *C* noted. (4) A vertical line is drawn through *C* perpendicular to *AB*, to meet either or all of the lines *OX*, *OY*, or *OZ*. (5) Then the pH value is given at the point where this line meets *OX*, *OY*, or *OZ*, according as the temperature of the experiment (*i.e.*, of both of the electrodes comprising the cell) is 18°, 25°, or 30° C. respectively.

It will be seen that the nomogram may be used for the hydrogen or quinhydrone electrode in combination with any calomel electrode between 18° and 30° C., for pH values ranging roughly from 2 to 12. The mean accuracy is about 0·02 pH, though for the most useful ranges, *e.g.*, for the saturated calomel electrode at 20° C. and pH 5–8, it is even higher. Values at temperatures between 18° and 25° or 25° and 30° are found with sufficient accuracy by proportion.

To use the nomogram for the conversion of pH values into millivolts it is necessary only to draw a vertical line from the point representing the pH value at the temperature concerned, and to place *C* at the point where this line cuts *AB*. The position of the electrode-indicator then gives the reading in millivolts, which would be obtained with a hydrogen or quinhydrone electrode with either of the three calomel electrodes.

If a piece of glass, celluloid, or other transparent material is used for the electrode-indicator a vertical line through *C* may be drawn or scratched on it, and the point where it crosses the required line seen at a glance. The most convenient form of this device, however, is the ruler recently placed on the market by Messrs. A. G. Gallenkamp, Ltd.

For those who wish to construct their own nomogram it should be mentioned that graph-paper ruled in millimetres is most convenient. Perhaps the best scales are 1 mm. to 2·5 millivolts for the line *AB* (both upper and lower scales), and 2·4 mm. to 0·1 pH for each of the lines *OX*, *OY*, and *OZ*. *CD* is 15·5 mm. and *CE* 36·5 mm.; while the angles made by *OZ* with *OX* and *OY* are 17° and 9° respectively. The lines *AB* and *OZ* are 30 mm. apart, and *X* is 80 mm. from *OZ*, so that the electrode-indicator, if made from transparent material as suggested above, should be at least this distance in width. The completed nomogram may be mounted on stiff cardboard and hung near the apparatus.

It should be noted that if it is intended to use only one combination of electrodes, the diagram is greatly simplified. Alternatively in such cases an ordinary graph may be plotted with millivolts as ordinates and pH values as abscissæ. The millivolt readings corresponding with any two pH values (say 2 and 12) are then found by calculation from the data supplied (see below), and the two points plotted and joined by a straight

line. This line represents the relation between pH values and millivolts at the temperature concerned, and if necessary, several such lines may be drawn corresponding with several temperatures. If large scales are taken, a high degree of accuracy is obtainable.

The data used for the calculations involved in the construction of the writer's nomogram are those of Table 4 (p. 144), and the necessary formulæ are given on pp. 37 and 47 for the hydrogen and quinhydrone electrodes respectively. The same table also gives some values of the product $0{\cdot}0001893T$ (where $T=t^\circ$ C.$+273$).

Other devices have been described,[50] but they are either less comprehensive, less simple, or less accurate than that given above. Books of tables [51] are also available giving the pH values to two decimal places for any voltage between 300 and 800 millivolts at intervals of 1° C. between 15° and 27° C. and at 37° and 38° C., but they refer only to the hydrogen and saturated calomel electrode combination.

Automatic and Recording Instruments.—These are finding extensive use in industry, but a description of the mechanism involved is outside our scope. The Cambridge instrument, in which a mechanical relay attached to the galvanometer moves the contact on the potentiometer slide-wire so as always to obtain a point of balance, has already been mentioned (p. 53), and there are numerous other types. The usual arrangement is a direct-reading instrument modified by one of the ordinary devices for recording the results on a scale calibrated directly in pH values. Lassieur [52] has described an instrument in which the potential to be measured is made to charge a condenser which is then discharged through a ballistic galvanometer whose scale is calibrated in pH values. A clockwork mechanism enables a determination to be made every minute with an accuracy of 0·07 pH. Müller and Partridge have described an automatic burette release controlled by an electric relay which may be adapted to enable sufficient acid or alkali to be added automatically as soon as the pH value changes beyond certain limiting values. Automatic methods are also sometimes used in electrometric titration (p. 112), and in the sugar industry (p. 125).

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PART III

THE COLORIMETRIC METHOD

CHAPTER I

THE THEORY OF INDICATORS AND AN OUTLINE OF THE METHOD

Outline of the Method.—In the colorimetric method for the measurement of hydrogen ions the solution to be examined is mixed with a small amount of a suitable indicator. The colour imparted to the solution by the indicator is in general always the same for solutions of the same pH value, whatever the composition of the solution. If the pH is changed slightly there is a corresponding slight change in the shade of the colour of the indicator-solution mixture.

If a number of buffer solutions are prepared having known pH values covering the pH range in which the unknown solution will fall, and the same quantity of the same indicator solution is added to each, a range of colours will be obtained, one of which exactly matches that of the test solution. This buffer solution will obviously have the same pH value as the solution. The method, of course, is in a sense indirect since it is based on the electrometric determination of the pH values of the buffers, but as accurate data are available there is usually no need for each worker to standardise his own buffers (see p. 22).

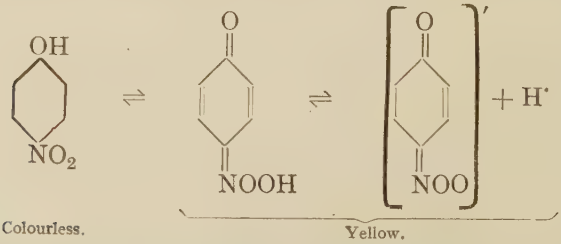
A wide choice of indicators is available, but as each indicator gives a sharp colour change only over a small pH range, it is necessary first to determine the approximate pH of the test solution by means of a universal indicator, and then to choose that particular indicator which shows the sharpest change in colour in the neighbourhood of the pH concerned. If the matching of the colours is carried out in one of the colorimeters designed for this purpose, an accuracy of 0·1 pH is obtainable. There are also modifications of the method which are very useful in particular cases, especially if an accuracy of only 0·25 pH is required (see p. 90).

Theory and Selection of Indicators

Definition.—In the widest sense an indicator is a compound which may exist in two forms having different colours. Here, however, where we are interested only in indicators which respond to changes in pH value we may define an *indicator* as *a compound whose solution changes in colour when its pH changes through a particular range.*

Indicators have been used to test for acidity since the time of Hippocrates, and litmus, the colouring matter from the red cabbage, is so well known that acids and bases were formerly defined in terms of its change in colour when mixed with them. It is only relatively recently, however, that numerous organic dyes have been found to have indicator properties, and the detailed study of these has shown that each dye has its own particular pH range for which the change in colour is most pronounced.

Theory of Indicator Action.—The oldest theory of any importance is due to Wilhelm Ostwald, who considered that indicators are ionised in solution just as weak acids and bases are, and that the unionised molecule has one colour, and the ions produced from it another. The extent of ionisation, and therefore of colour change, is regulated by the amounts of acid or base added. Hantzsch's chemical or *chromophoric theory* is an extension of Ostwald's theory, and maintains that the change in colour is not due to ionisation, but to a reversible change in chemical constitution produced by the addition of $H^{\cdot}$ or OH' ions. For example, phenolphthalein is a lactone in acid solution, and is colourless, whilst on the addition of an alkali the lactone structure is broken and a quinone structure produced. Quinone structure is associated with the production of colour, and, of course, alkaline phenolphthalein is red. The colour change of *p*-nitrophenol is represented by the change in constitution shown in the equation:



Examples of change in colour corresponding with changes in constitution might be multiplied. Kolthoff,[1] however, considers

that neither Ostwald's nor Hantzsch's theory alone explains indicator action.

The former does not account for all the known facts, *e.g.*, the solid salt of phenolphthalein, which, of course, cannot be regarded as ionised, is red, whereas according to the theory it should be colourless. The latter theory merely indicates that a change in colour is accompanied by a change in constitution, but does not explain the cause of the former. Nor does it explain the influence of the pH value. There are also objections to Wolfgang Ostwald's [2] theory that the colour change is due to a change in the degree of dispersion of the indicator, and also to Baly's purely physical theory.

Kolthoff (*loc. cit.*) establishes a fairly satisfactory compromise by assuming that indicators may exist in two forms, having different colours: (1) a *pseudo* or *normal* form, and (2) an *ionogenic* (*i.e.*, *aci* or *baso*) form. The colour change is then governed by the equilibrium:

$$\text{pseudo or normal form} \rightleftharpoons \text{ionogenic form},$$

and an indicator is defined *as a weak acid or base whose ionogenic or aci* (*or baso*) *form has a different colour from that of the pseudo or normal form.*

In the case of *p*-nitrophenol (p. 78), which is a weak acid, the colourless form $C_6H_4.NO_2.OH$ is the pseudo or normal form, whilst the aci form is the nitrolic acid with the quinone structure, $O.C_6H_4.NOOH$. This can be ionised like an acid to give a $H^{\cdot}$ ion:

$$O.C_6H_4.NOOH \rightleftharpoons O.C_6H_4.NOO' + H^{\cdot},$$

and hence is called an aci compound. In general,

$$InH \rightleftharpoons In' + H^{\cdot}.$$

Analogously, indicators which are weak bases give a baso compound ionised into OH' ions and a positively charged residual ion, thus:

$$InOH \rightleftharpoons In^{\cdot} + OH'.$$

In general, for both types of indicator:

$$\text{pseudo acid (or base)} \rightleftharpoons \text{aci (or baso) form} \rightleftharpoons H^{\cdot} \text{ (or } OH') + \text{aci' (or baso}^{\cdot}).$$

This theory covers Hantzsch's ideas because the ionogenic and the normal forms are given different constitutions, while it only differs from Ostwald's in that it is the ionogenic form (instead of the actual ions) which has a different colour from that of the pseudo form.

Colour Change and pH Value.—Kolthoff thus explains not only the exceptions to Ostwald's theory, but also the effect of

pH on the colour change. If the indicator is an acid, and we apply the mass action law to the reactions:

$$\text{normal} \rightleftharpoons \text{aci} \rightleftharpoons \text{aci}' + \text{H}^{\cdot},$$

we have $K = C_{\text{aci}}/C_{\text{normal}}$, and $K_{\text{aci}} = C_{\text{H}^{\cdot}} \cdot C_{\text{aci}'}/C_{\text{aci}}$,

i.e., $$K_{\text{HIn}} = K_{\text{aci}} \cdot K = \frac{C_{\text{H}^{\cdot}} \cdot C_{\text{aci}'}}{C_{\text{normal}}}.$$

This simple relation is also obtained directly from Ostwald's theory by applying the mass action law to the equation:

$$\text{HIn} \rightleftharpoons \text{In}' + \text{H}^{\cdot} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

only according to our revised ideas, $C_{\text{In}'}$ has been replaced by C_{aci}'.

K_{HIn}, however, is not the true dissociation constant, but that obtained by multiplying the true dissociation constant and the constant (K_{aci}) for the equation relating the normal and aci forms.

For simplicity, consider only equation (1) and apply the same reasoning used for ordinary acids (p. 7).

Then $$K_{\text{HIn}} = \frac{C_{\text{H}^{\cdot}} \cdot C_{\text{In}'}}{C_{\text{HIn}}}.$$

If $C_{\text{In}'} = C_{\text{HIn}}$, the reaction has proceeded halfway, *i.e.*, the colour has half changed over, and $K_{\text{HIn}} = C_{\text{H}^{\cdot}}$.

By double differentiation of the equation (p. 15)

$$\text{pH} = \text{p}K + \log \alpha/(1-\alpha)$$

we obtain for the rate of increase of α with respect to pH, $d\alpha/d(\text{pH}) = \alpha(1-\alpha)$, and thence $d^2\alpha/d(\text{pH}) = 1-2\alpha$. When the rate of increase is a maximum this equals zero, and $1-2\alpha = 0$, or $\alpha = \frac{1}{2}$. *The maximum rate of change of the indicator is therefore at its half-transformation point.*

In practice this is not strictly true, because the eye is influenced more by the more dominant colour and cannot differentiate small changes in colour at the critical point. Thus, phenolphthalein may appear red after it has become colourless.

We see, therefore, that the colour change is definitely a function of the hydrogen ion concentration, and that at the pH value corresponding with the point of half-transformation of the indicator the change is sharpest, because equal amounts of both coloured forms of indicator are present. Either side of this point one or other is present in excess.

The region between the two limiting pH values over which any change in colour is perceptible is the *transition interval* of the indicator. A typical neutralisation curve of an indicator which

changes at about pH 5 to 7 (*p*-nitrophenol) is shown in Fig. 25. It is seen that the sharpest change in colour with change in pH is at pH 6. Below pH 5 and above pH 7, however, the addition of acid and alkali, respectively, produces practically no colour change, because a large excess of one or other colour is already present. Such curves are not usually symmetrical, because the intensities of the two colours are seldom developed to the same extent for the same concentration of indicator.

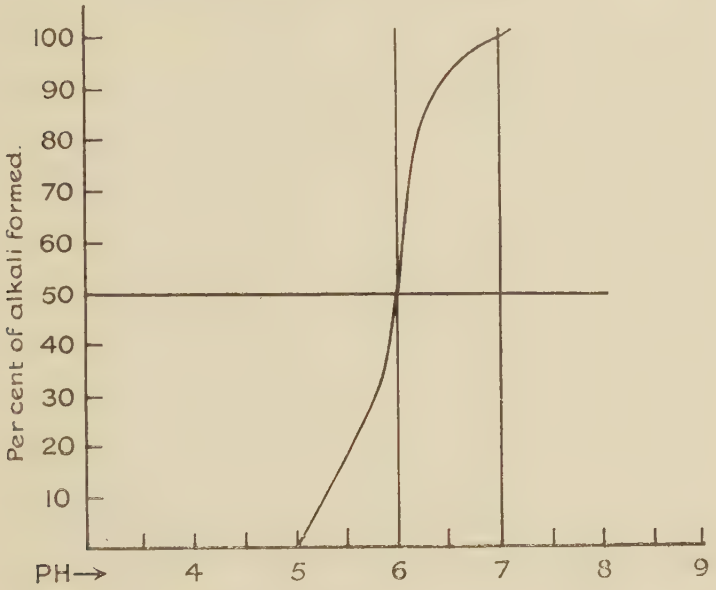


FIG. 25.

Choice of Indicators and Effect of Concentration.—Curves of this type, or simply a list of the dissociation constants of indicators, are a valuable guide to a choice of the latter, for they enable the behaviour of an indicator over a particular pH range to be seen at a glance. In Tables 5 and 6, on p. 145, the properties of a number of indicators are tabulated together with useful data concerning their use, and though these represent only a small percentage of the indicators proposed from time to time for various purposes, they are recommended for general use mainly on account of their brilliant transition-colours, and because ample information as to their behaviour is available.

Indicators which have a transition-interval between pH 3 and 11 usually give a sharp change for strong acid-base titrations.

Those outside this range require a considerable excess of acid or alkali to produce a change in colour, and are useless for general purposes. Cresol red, however, which has an acid range of pH 0·2–1·8 (red to yellow), has been found useful for adjusting solutions of strong acids. The colour of the ideal indicator should be a function only of the numbers of H· and OH′ ions present, and the colour change should be sharp.[4] In the selection of indicators attention should be paid to the rate and nature of the change in colour over the range concerned, and a certain amount of overlapping in the ranges of the indicators of the series should be ensured.

The indicators tabulated on p. 145 have been selected because they cover a wide pH range, and because as a series they show the minimum number of disadvantages an indicator may possess. Those proposed by Clark and Lubs (Table 5) belong to the sulphone phthaleins. They are well suited for use in the drop-ratio method (p. 93), and the relative change of colour is greatest at the pH of the half-transformation point (pH=pHIn), though a small colour change is more easily seen on the acid side, since the alkaline side is usually more highly coloured. Further, brom phenol blue and brom cresol purple are dichromatic (p. 83), and the list is therefore supplemented by Cohen's indicators, bromcresol blue, and chlorphenol red. Brom thymol blue is particularly useful to replace phenolphthalein in red-coloured solutions, as it turns blue with alkali. A few other miscellaneous indicators are included because they are generally useful, and references are made (also in the Bibliography, p. 101) to other reputable indicators which some may care to test (*e.g.*, Sörensen's indicators, Michaelis and Gyemant's one-colour nitrophenol indicators, and quinine, which is a universal indicator in ultra-violet light).

Apart from their chemical differences, indicators fall into two main groups, viz. one- and two-colour indicators. Those of the one-colour type (*e.g.*, phenolphthalein) change from colourless to coloured, or *vice versâ*, whilst the others change from one colour to another, with change of pH. Obviously the transition-interval of an indicator will depend to some extent on its concentration, since if the indicator is not present in sufficient quantity the colour will not be sufficiently intense to enable the change to be seen. The change is therefore dependent in turn on the solubility of the indicator, and it can be shown that the colour-change interval is greater for the more soluble indicators. For this reason the quantities of indicator to be added (Table 5) are important.

With one-colour indicators the amount of the coloured form is proportional to that of the undissociated indicator. But here

we are dealing with the gradual increase or decrease in intensity of one particular colour, and so a definite amount of the coloured form must be present before it can be perceived. The concentration or solubility is therefore again of importance, though not to the same extent as in the case of two-colour indicators where the colours of the two forms may differ in intensity, and the visible range on the less intense side of the half-transformation point be correspondingly reduced.

Certain indicators (*e.g.*, brom phenol blue) show different colours according to the depth of solution used. This property is known as *dichromatism*, and is due to reversal of the intensities of the colours concerned for different thicknesses of the liquid. It may be eliminated, if necessary, by the use of a screen painted with an acid solution of phenol red and placed in front of the light. Fluorescent substances are also used as indicators (*e.g.*, iodo-eosin, quinine [13], naphthol), and are very sensitive in dilute solutions.

The effects on indicator action of other conditions are discussed under the heading of errors and technique (p. 97).

Colorimetry

There are certain principles underlying the comparison and matching of colours which help us to arrive at the most suitable instrument for this purpose.

Light.—What we call light (daylight or sunlight) is actually a mixture of the colours of the sun's spectrum (red, orange, yellow, green, blue, indigo, and violet). Sunlight is actually split up into a band of these colours when it is passed through a prism, and the rainbow, in which rain plays the part of the prism, is a demonstration of this on a large scale. On the other hand, if rays of light of these same colours are focussed on one spot, the spot will appear white. This does not apply to mixtures of pigments, because these are seldom pure in the colorimetric sense.

When, therefore, we say this paper is white, we mean that it reflects all the constituents of daylight to equal extents, so that the combined effect on the eye is, approximately, that of daylight. Red paper, however, reflects only red rays to the eye and absorbs the remainder (orange, green, blue, etc.). If we hold a solution of an indicator up to daylight and add an acid or alkali so that it changes colour, the colour-change as the eye sees it is the result of rays of certain colours being cut off or absorbed, while others are allowed to pass.

The source of light is therefore of great importance in matching colours, since a solution which appears red in daylight would

have no colour in blue light because it transmits only red rays, and *vice versâ*. In the ideal case a colour is best viewed in light the rays of which it transmits, but in practice it is more convenient to have a source of light which provides for all cases, and daylight is obviously the best standard. It may be taken, then, that the ideal source of light is north daylight reflected from a white matte surface. Direct sunlight, if obtainable, is liable to produce a glare which renders matching difficult. On the other hand, the blue-coloured electric " daylight " bulbs which fit into the ordinary holders, or " Fullolite " lamps, may be used as a substitute for daylight at night time, although the rays they emit are not quite the same as those of true sunlight. Ordinary electric light may be used with the Clark and Lubs indicators. The main point is that both test solution and standard must be matched in the same source of light and under the same conditions.

Theories of Colour.—When colours are to be matched, the question at once arises how can a composite quality such as colour, which cannot be split up by the eye into its components, be expressed in figures or symbols ?

According to Helmholtz (1867) all colours are made up of mixtures in various proportions of three primary colours, red, green or yellow, and blue. If, therefore, we can determine the proportions of each of these colours in the colour we are examining we have a means of recording the actual value of the mixed colour so that it may be reproduced at will without reference to a standard. Many colorimeters [5] are designed on these lines. Thus optical devices have been adopted to combine varying quantities of light coloured by passage through three filters (usually coloured glass or gelatin), and to focus on them on a point immediately adjacent to the test solution. The proportions of the colours are then varied till the resulting colour matches that of the test solution.

Three obvious difficulties arise. Firstly, how can the three filters providing the primary colours be standardised so that they are reproducible and always give the same values in different instruments ? Secondly, although two colours may match as far as their contents of the primaries is concerned, they may differ greatly in brilliance or hue. This difficulty is often overcome by the use of filters of a " neutral " colour, such as would be produced by mixing exactly equivalent quantities of the three primaries. These serve to cut off light but not colour, and are added to whichever of the two colours under comparison appears the brighter. The third and most important difficulty is the personal factor, which it is almost impossible to eliminate. Different observers have colour senses which respond more

readily to one primary colour than to another, and it is often not easy for several workers to reach an agreement on the same colour.

Although the Helmholtz theory or its modifications is usually accepted, colorimeters based on other principles have been designed with the object of overcoming the above difficulties. For example, in Ostwald's system [6] colours are expressed in terms of grey (*i.e.*, black plus white). The black component is obtained by examining the colour in light of its own colour and matching the grey produced against one of a standard series of greys. The white component is obtained in the same way by using the colour *complementary* to that of the test solution, *i.e.*, the colour which when mixed with it would give white. The advantage is that only greys are matched, and the luminosity difficulty is also eliminated.

These considerations apply equally to the colorimetric measurement of hydrogen ions, but in this case, fortunately, we are able to eliminate all but the personal factor for the simple reason that the colours are not expressed in terms of their primaries, but are matched by comparison against standards of known value. Apparatus for the former purpose has, however, been designed, and the method, though inconvenient for rapid use, is more sound scientifically.

Spectrophotometric methods, in which the light traversing a solution of the indicator is split up by a prism into its constituents, are used for the determination of the end-points of indicators. The emergent light appears as a succession of bands which change in a manner characteristic of each indicator when the end-point is reached. Since absorption is measured only for the narrow wave-length line it is characteristic of the colour, and the effect of coloured impurities is overcome. The method is mainly of academic interest, but it has been used to obtain the indicator data on which the practical worker relies, and is therefore of interest.

Simple Colorimeters.—The theoretical foundation on which all colorimetry rests is expressed by *Beer's law*, which states that when a ray of light passes through a layer of liquid containing a coloured substance, the intensity of the emerging ray (I) is inversely proportional to the concentration of the coloured substance (c), and to the thickness of the layer (l).

Thus, for example, a layer 10 cm. deep of a 20 per cent. solution has the same absorption as a layer 5 cm. deep of a 40 per cent. solution. The two solutions of the same hue, one of unknown concentration and one a standard, are placed in the colorimeter and the thickness of liquid required to produce the same intensity of absorption is found. By Beer's law, $I \propto 1/c \propto 1/l$, or $I = k/c \,.\, l$, where k is a constant. For the standard, $I_1 = k/c_1 \,.\, l_1$,

and for the unknown $I_2 = k/c_2 \cdot l_2$. Since at the point of balance

$$I_1 = I_2,$$

therefore

$$c_1 \cdot l_1 = c_2 \cdot l_2.$$

This is the expression of Beer's law, for if l_1 and l_2 are measured by the colorimeter and c_1 is known, c_2 may be found. The law always holds unless the substance concerned undergoes changes (*e.g.*, association or reaction) in solution.

In its simplest and most convenient form the colorimeter, or more strictly the comparator, consists of a closed wooden box with vertical holes in which to stand test-tubes, and horizontal holes corresponding with each tube by means of which they may be compared. The importance of using similar tubes all of which have the same internal and external diameters requires no emphasis, since the light must pass through the same amount of glass and solution in each case. It is necessary only to hold the box against the light and find the tube the colour of which most closely matches that of the test solution. There are ingenious modifications designed to eliminate the colour or turbidity of the solution, and these are described in the next chapter.

It will be seen that the colorimetric measurement of hydrogen ions is an extremely simple and convenient process, and one capable of a fairly high degree of accuracy when properly standardised. Its limitations and its dependence on the electrometric method should, however, always be kept in mind.

CHAPTER II

PRACTICAL

Indicators

Preparation and Storage of Indicator Solutions.—The indicators given in Table 5, p. 145, are easily obtainable in the solid state suitable for immediate use. Fairbrother,[8] however, gives notes on their preparation which may be of interest.

To prepare 100 c.c. of solution, the correct quantity of indicator (Table 5) is ground in a small mortar with the volume of 0·05*N* sodium hydroxide solution stated, and sufficient alcohol (40–60 c.c.) to dissolve the dye. The mixture is then diluted to 100 c.c. with water so as to give a solution of the specified strength, and filtered if turbid. The alkali is added with the object of exactly neutralising the dye where this is necessary, and so producing the colour at its half-change point.[9] Otherwise a portion of the test solution is used up for neutralisation of the indicator, and a small error introduced. Such solutions are not permanent and should be replaced every few months.

Where badly-buffered solutions are to be used, and a high degree of accuracy is required, it is best to adjust the indicator to its half-transformation point by the electrometric method, or else to add the alkali until the colour exactly matches that of a mixture of the indicator and a buffer solution having the pH of its half-transformation point.

Suitable *water* is prepared by boiling a litre of distilled water till 700 c.c. remain. This is stored in pyrex vessels out of contact with air. Where determinations have to be carried out in the acid air of the laboratory the containing vessels may be filled with air drawn through lime water.[10]

Universal Indicator.—The individual indicators given in the table each cover only a narrow pH range, and it is convenient to have a mixture of indicators which will give the pH of any solution from 1 to 12, even if the value is only approximate. Such a solution might be prepared in relatively large quantities, and used as a preliminary test to ascertain which of the special indicators in the table is the most suitable for the particular purpose.

The British Drug Houses, Ltd.,[11] supply an excellent mixture which contains methyl red, naphtholphthalein, phenolphthalein, brom thymol blue and cresolphthalein, but a very useful substitute may be prepared by dissolving 0·1 grm. methyl orange, 0·4 grm. methyl red, 0·4 grm. brom thymol blue, 0·32 grm. naphtholphthalein, 0·5 grm. phenolphthalein, and 1·6 grms. cresolphthalein in 100 c.c. of 70 per cent. alcohol (Van Urk [12]). One drop is added to 10 c.c. of test solution and the colours obtained for various pH values are red-orange (3), yellow-orange (5), yellow (6·5), green (8), green-blue (9), violet (11), and red-violet (12). It will be noted that the colours follow the order of the solar spectrum for ascending pH values. Quinine is a fluorescent universal indicator in ultra-violet light.[13]

Colour Standards

Preparation.—The colour standards are prepared by addition of the amounts of indicator given in the table to 10 c.c. of buffer solution (p. 22). The amounts of indicator to be added differ on account of the different tinctorial powers of the dyes. A test-tube of hard borosilicate glass or pyrex marked at 10 c.c. is very suitable. Test-tubes should be dried, but not by heat, and they should be rinsed with the solution to be used. If they are filled completely, immediately stoppered, and the corks paraffined outside so as to eliminate carbon dioxide from the air, the chance of the glass dissolving and producing alkalinity is minimised. On the other hand, the use for colour standards of vessels paraffined inside should be avoided if possible, as acidity may be produced from the wax, and the same applies to layers of wax sometimes placed on top of the liquid surface. It is, of course, important that all the tubes used for the standards or test solutions should be for the same size, colour, and diameter. These may be selected by pouring 10 c.c. of water into a number of test-tubes and picking those in which the level is the same; $\frac{5}{8}$ in. is a convenient diameter.

Although buffer solutions themselves may be preserved from mould growth by the addition of 2 c.c. per litre of a saturated solution of mercuric chloride, or of toluene, and so be stored unchanged for very long periods of time, the shade of colour produced on addition of the indicator is apt to fade after a few months. As the whole series may fade to the same extent, the change may not be apparent when a measurement is being made, and it is as well to renew thymol blue and methyl red standards every few weeks, and brom thymol blue and brom phenol blue every three months, though brom cresol purple should last at

least six months. The rate of fading is greatly diminished if the standards are stored in the dark.

Permanent Standards.—Mixtures of inorganic salts may be prepared so as to show exactly the same colours as the mixtures of the dyes and buffer solutions, but they are much more stable and may be kept indefinitely. They must be used with caution. The author's experience is that much of the published data is untrustworthy, and it is well for each observer to prepare his own standards. Where nitrophenol indicators are used (p. 82), chromate and dichromate solutions alone make excellent substitutes,[14] but for the Clark and Lubs series, mixed solutions of salts of cobalt (red) and of copper (blue) with dichromates (yellow) must be used.

Table 7 on p. 146 gives a series of such solutions devised and tested by the author, and based partly on the data of Bruère and of Taub.[15] Two coloured solutions matching the extreme acid or alkaline indicator colours are prepared, and mixed in graded proportions exactly as in Gillespie's drop-ratio method (p. 93). When adjusted for the idiosyncrasies of the individual vision these make excellent permanent standards, though spectrophotometric examination [16] indicates that their tints may differ from those of the corresponding indicators to extents not always appreciable by the human eye.

Where a Lovibond tintometer is available, and it is required always to work to one or two fixed pH values, it is an excellent plan to note the combination of red, yellow, and blue Lovibond glasses required to reproduce the colour of the standard representing the pH required. A truly permanent standard is thus obtained. Where these glasses are not available, the method devised by the author may be used, in which the necessary volume of mixed inorganic salt solutions is added to a hot mixture of glycerol and water (2 : 1) in which gelatin is dissolved. The colour mixture is cooled and allowed to set between two microscope slides separated by a slip of glass 1 mm. thick, and a permanently coloured transparent slide corresponding with a definite pH is thus obtained.

Indicator Papers [17].—These are best prepared by soaking strips of ash-free filter paper in a saturated solution of the neutralised indicator, and drying them evenly at a low temperature. At the best they are unsatisfactory, and can only be used for gases or for the approximate adjustment of the pH value of coloured or turbid solutions. The author prefers to use sized papers, although these take a few minutes to attain their full colour. Unsized papers show rings of colour produced by different concentrations of dye adsorbed on different portions of the paper. Here, again, it is often convenient to prepare standard test papers which have been soaked in buffer solutions

of the required pH, and to calibrate the papers according to the purpose for which they are to be used.

By means of Wulff's method [19] an accuracy of 0·2 pH is claimed over the range pH 1·0–12·5. Transparent strips of material impregnated with indicator are soaked in the test solution for two minutes. The colour changes, and is then matched against colour standards. The method is not well known in this country, but if the standards are accurate, and the strips are properly prepared, it should be useful for opaque or turbid solutions, especially those encountered in industrial processes (p. 129), for the strips may be washed rapidly with distilled water without removing any indicator. On the whole, however, colour standards which are supplied by a firm and cannot be checked by the user are always suspect after a time and are not recommended.

Comparators

This term in its widest sense includes all apparatus in which colours are matched or compared against standards and is to be distinguished from *colorimeters*, which is a general term including comparators, and covering instruments used to determine the concentration of colour in a solution as distinct from its tint, and other apparatus for the colorimetric analysis or examination of colours.

Comparators may be grouped in two main classes, viz. (1) Those in which the colour is matched against colour standards representing different pH values and prepared as described above. (2) Those in which simple devices are used to combine in varying proportions the two extreme colours produced on adding an excess of (*a*) alkali, or (*b*) acid to the indicator.

Nessler Tubes.—These are the simplest form of comparator, and since they are easily obtained they are very useful for rapid measurements. In Cameron's method [19] 25 c.c. of the test liquid and 1 c.c. of 0·004 per cent. indicator-solution are mixed and diluted to 50 c.c. in one cylinder. The other contains 1 c.c. of indicator and the buffer solution without the standard acid or alkali, and the latter is then added from a burette until the colours exactly match. It is necessary that each cylinder should contain the same amount of indicator, and the test solution should be well-buffered or dilution will change its pH value. Also, there should be the same depth of liquid (50 c.c.) in each cylinder when the match is made. The table of buffers on p. 142 gives the pH for different amounts of acid or alkali.

Block Comparators.—These are also a very simple type and easily home-made. The instrument made by the British Drug Houses, Ltd., is shown pictorially in Fig. 26 and in plan in Fig. 27.

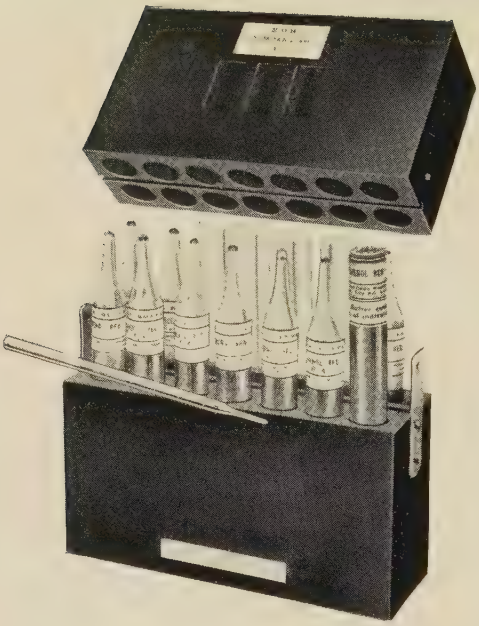


Fig. 26

B.D.H. Comparator

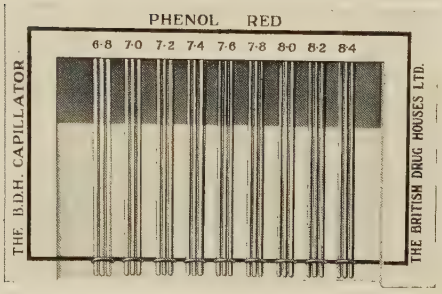


Fig. 29

B D.H. Capillator Card

It is a wooden block or closed box about $4\frac{1}{2}$ ins. long, 3 ins. wide, and $3\frac{1}{4}$ ins. high, with three pairs of holes (AA′, BB′, and CC′) bored vertically to take the standard test-tubes. In the front of the instrument, near the base, are three more holes about $\frac{1}{2}$ in. in diameter, bored from back to front, so that when the comparator is placed against the source of light (L), the eye (E) looks through either or all of the pairs of tubes along the dotted lines. The block is painted black throughout to avoid internal reflection, and the portable models are provided with a lid which contains a pipette and may also serve as a stand for spare tubes.

With clear and colourless liquids the holes in the back row

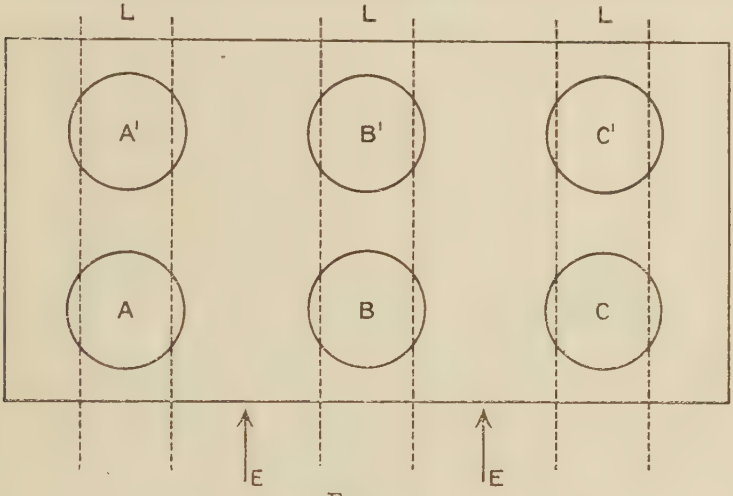


FIG. 27.

(A′, B′, C′) remain empty, and the test solution and indicator are placed in B. Two standards whose pH values differ by 0·2 (or less if the colour difference is appreciable) are then selected and placed in A and C, so that there is an even gradation of colour in passing from A to B and to C. The pH value of the solution in B is then the mean of those of A and C.

With slightly turbid or coloured liquids the solution may be diluted if it is a good buffer. The colour or turbidity may also be compensated by placing water in the tube B′, and the test solution *without the indicator* in tubes A′ and C′. In this way the light travels in all three cases through what amounts to the test solution, and a solution of the indicator in water.

Those who favour a more refined instrument may easily construct one on the lines of that described by McCandlish and Hagues [20] and

shown in plan in Fig. 28. Light from a 40-watt " Fullolite " lamp (L) is reflected from each of the mirrors M and M′ through (1) the tubes AA′ (containing water, and the test liquid plus indicator respectively); and (2) through BB′ (containing the test liquid

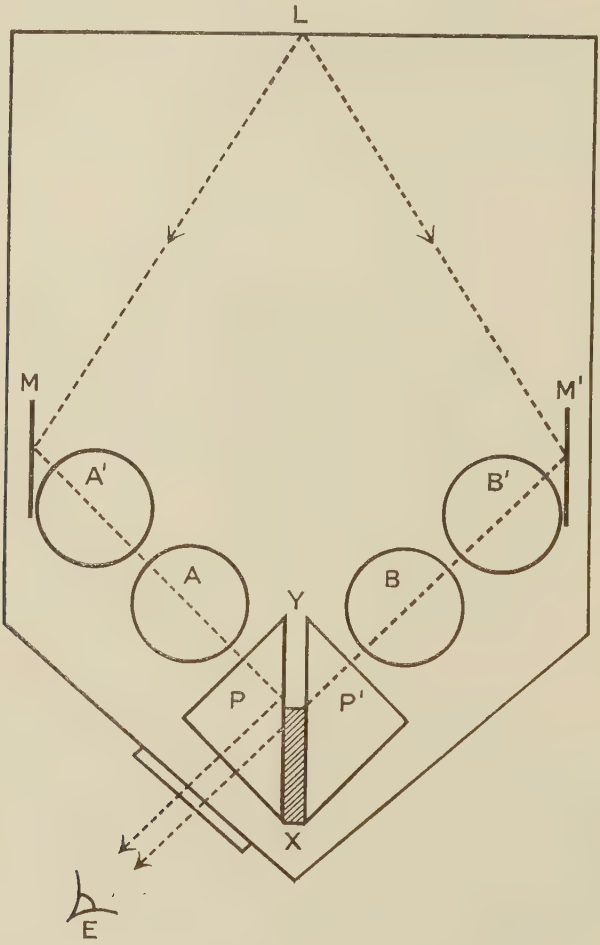


Fig. 28.

without indicator, and a standard solution respectively). PP′ are ordinary right-angled prisms placed with their hypotenuses in contact, the front halves (X) only being cemented with Canada balsam, so that the back halves are separated by an air-gap (Y). The ray from M′ passes straight through B′, B, P′ and P to the eye

E, whilst that through M, A′, and A is internally reflected in P so that the rays emerge together. The tubes thus appear to be next to one another, and can be matched with much greater accuracy. The whole system is contained in a box 3¾ ins. deep, painted dull black.

The Capillator.—This useful device, which was suggested by Ellis,[21] and is made by the British Drug Houses, Ltd., must also be mentioned because it is useful for rapid pH measurements, and because the whole apparatus fits the pocket and is very suitable for field work.

As Fig. 29 (p. 91) shows, each standard consists of sets of three capillary tubes containing the coloured liquid, mounted together on a white card so as to form a strip about ¼ in. wide. Each card has a number of these sets corresponding with differences of 0·2 in the pH of the indicator concerned. A similar capillary tube provided with a small rubber bulb is used as a pipette to measure out equal quantities of test solution and indicator which are then mixed in a watch-glass, again drawn up into the pipette, and the colour of the liquids matched against the appropriate standard. The cards are provided with a slot so that reflected or transmitted light may be used.

Apart from portability and speed the advantages of the method are that the thin layer of liquid and the concentrated indicator-solution enable slightly coloured or turbid liquids to be tested, and that measurements may be carried out with one drop of solution. On the other hand, the use of a volume of indicator equal to that of the test solution will introduce an error if badly-buffered solutions are used, while the life of the standards is limited (p. 88), and the indicators, which are concentrated, require to be specially prepared. The standard tubes are fragile and must be handled with care. A compensation cell, equal in thickness to the diameters of the capillary tubes, is now also obtainable. For highly-coloured liquids it is filled with a two-fold dilution of the test-liquid, and the colour of the standard viewed through it, the capillary tube containing the test solution being viewed through clear glass (see Soils, p. 106).

Drop-Ratio Comparators.—If the equation

$$\mathrm{pH} = \mathrm{p}K + \log \alpha/(1-\alpha) \quad \text{(see p. 15)}$$

is applied to an indicator, α may be taken as the *degree of transformation*. Gillespie[21] assumed that the light is absorbed independently by the two coloured forms of the indicator, and therefore that it is immaterial whether these are mixed in the same vessel or contained in two separate vessels and placed in the same line of light. It is therefore possible to imitate an indicator colour corresponding with a particular

pH by dividing the indicator in the proper proportions between two vessels, one containing an excess of acid, and the other an excess of alkali. Thus to obtain a 70 per cent. colour change seven drops of indicator are placed in one vessel and three in the other, whilst for a 90 per cent. change the ratio of drops is 9 : 1. Table 8 on p. 147 shows the drop-ratios corresponding with different pH values as determined from the dissociation curves of the indicators.

The method, though not highly accurate, is very useful, since it eliminates buffer solutions and is particularly applicable to the Clark and Lubs indicators. The only apparatus required are eleven pairs of test-tubes as similar as possible placed in a double test-tube stand. They are marked at 5 c.c., and 1 to 9

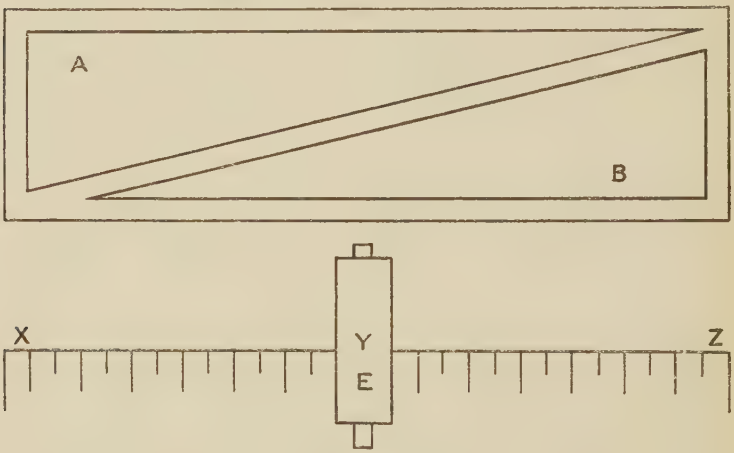


Fig. 30.

drops of indicator-solution placed in the front row according to Table 8, and 9 to 1 drops in the same order in the back row. A drop of 0·2 per cent. sodium hydroxide solution is then added to each of the former (two drops for thymol blue), and a drop of the appropriate acid solution (see Table 8) to the back row, and the tubes filled to the 5 c.c. mark with water. Each pair is clipped together, labelled with its pH value, and used in the comparator with 5 c.c. of test solution containing 10 drops of indicator-solution, compensation for colour, etc., being made by the usual method. For one-colour indicators only one row of standards is required.

A convenient apparatus for this method is McCrae's double wedge [23] shown in Fig. 30. Two right-angled glass cells, A and B,

are required, and are placed on a rectangular base so that their hypotenuses coincide. In A is placed an acid solution of the indicator, and in B the alkaline indicator, and by moving the observation tube E along the scale XYZ the position may be found where the two extreme colours are mixed in the correct proportions to match the colour of the test solution. The scale division is graduated so that X is the pH of the extreme acid colour of the indicator, Y its change-over pH value, and Z the pH corresponding with complete alkalinity.

Another convenient apparatus, which may be more easily constructed, has been suggested by Gillespie [21, 24] and is shown in Fig. 31. A and D are fixed empty glass observation tubes, while B is a

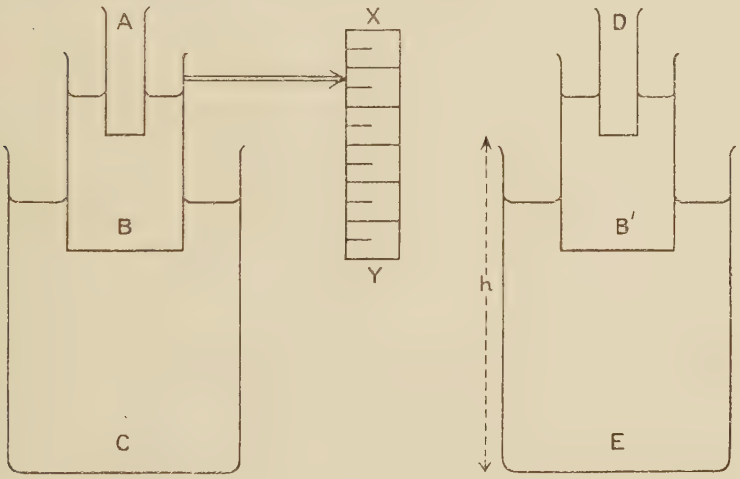


Fig. 31.

movable glass vessel containing the acid indicator and carrying a pointer which moves along the pH scale. C contains the alkaline indicator. The pointer should indicate the alkaline pH when the bottom of B touches A, and the acid pH when it touches C. By moving B up and down the proportions of acid and alkali are varied at will. E, which contains the test solution and indicator, the same depth, *h*, of which is viewed through D as through A, may be used as a titration-vessel. Nessler tubes in clamps may be used for A and D, and the author prefers to insert the tube B′ containing water to balance the optical effect of B. Prisms may be used to bring the fields of colour close together as in the apparatus described on p. 92.

Electrical Comparators.—There is little doubt that the comparator of the future will be electrically operated and

recorded, and that the human element, with its inevitable idiosyncrasies of judgment, will be eliminated. Such instruments have now advanced beyond the experimental stage, and as they are not difficult to construct, a brief description of the simplest type will be given.

When selenium or, better, the alkali metals or their oxides are illuminated, they emit a stream of electrons which will conduct a current (*photoelectricity*). If, therefore, a photoelectric substance is made one electrode of a cell, and the cell connected in series with an accumulator and a current-indicating instrument (galvanometer), as shown by the galvanometer, a current will flow through the circuit when the cell is illuminated.

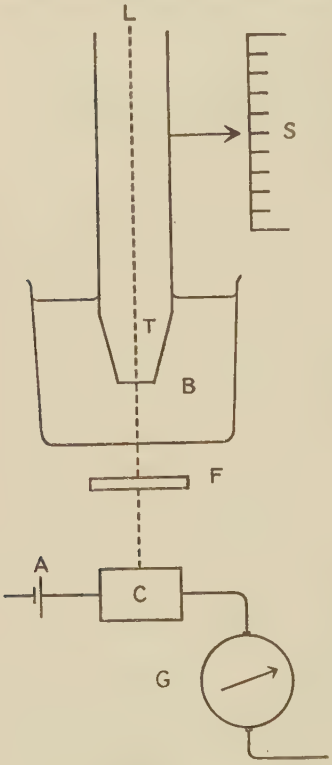


FIG. 32.

A simple instrument [25] is shown in Fig. 32. A parallel beam of light from L passes down the vertical tube T, through the indicator and solution in the glass vessel B, and is focussed on the sensitive electrode of the photoelectric cell C in series with an accumulator A and a milliammeter G. T, which slides vertically, is lowered until it touches the bottom of the vessel, and a suitable filter F placed in position. The milliammeter then gives a zero reading, after which F is removed and T raised until a zero reading is again obtained. The upward displacement is measured on the scale S and is an inverse measure of the colour-intensity of the liquid.

In Bruère's instrument [26] the thickness of solution is fixed, and the deflection of the galvanometer for the test solution plus indicator is expressed as a percentage of that obtained with distilled water alone. These values are then plotted against the pH values of the solution and a curve characteristic of each indicator obtained. In other cases [27] the photoelectric cell itself is used as a source of current and the accumulator eliminated. This involves amplification of the cell current by means of a valve circuit.

The disadvantage of these methods in their present state is that the apparatus needs to be standardised or calibrated for the particular purpose for which it is used. It is only with an indicator (such as phenolphthalein) which changes from colourless, or almost colourless, to an intense colour, that an absolute reading can be obtained, since in this case the cell may be adjusted so that the appearance of the colour cuts off the current completely. Such methods, of course, only give the pH of the end point, but they are useful for the automatic control of titration, and the General Electric Co., which makes a cheap and efficient photoelectric cell, has carried out successful experiments of this type (p. 112). The use of special colour filters also, is a disadvantage, but is rendered necessary by the fact that photoelectric cells are more sensitive to light of one colour than of another. The filter is chosen according to the purpose and indicator for which the apparatus is required. Such instruments appear to have a future, especially for the purpose of automatic titration to a particular pH value, and they will probably have many uses in industry or for routine work.

Descriptions of the more expensive and elaborate types of instrument are beyond the scope of this book, and references must be made to the literature.[28] They are usually colorimeters which may be used as comparators and have a high degree of optical precision. Though they may be capable of measuring differences in colour corresponding with 0·01 pH, the experimental errors of the colorimetric method are so great as to render this degree of accuracy meaningless unless special precautions are taken. The apparatus described above should meet most needs and should be chosen with regard to (1) whether buffer solutions are to be used; (2) whether many or few measurements are to be carried out at a time; and (3) the degree of accuracy required. Where many measurements are to be made fairly accurately it will obviously pay in the long run to construct a more elaborate apparatus; otherwise the test-tube rack type will suffice.

Technique and Sources of Error

The following section will be devoted to hints on the technique of the method with special reference to common sources of error and means of allowing for or eliminating them.

The Salt Error.—If the test solution contains large quantities of salts (*e.g.*, sodium chloride in sea-water or salts produced by neutralisation) the "salting-out" effect familiar to dyestuff chemists may occur with respect to the indicator, and a false colour be produced. In general, neutral salts tend to change the colour in the direction of the neutral point. According to

Kolthoff the salt may affect either the optical absorption of the coloured forms of the indicator, or it may influence the equilibrium established between them.

The corrections for the salt errors of the indicators recommended above are shown in Table 6 on p. 146, and are taken principally from the data due to Kolthoff [1, 29] (*loc. cit.*). Such data may be obtained (1) by calculation from Debye and Hückel's theory of strong electrolytes ; (2) by standardisation against the electrometric method, which as already pointed out (p. 69) is not entirely independent of this source of error, but may be used to determine it from the change in pH value produced on addition of the salt to a solution of known pH ; (3) by noting the change in pH (*i.e.*, in colour) when the salt is added to one of a pair of colour standards containing the indicator concerned.

Phenol red, thymol blue, brom thymol blue, and brom cresol purple have almost the same errors for concentrations of salt less than 0·1*N*. Thymol phthalein has a large error for pH 8 to 10, and a smal error for pH 1 to 3. Brom phenol blue, cresol red, litmus and tropaeolin-*O* have large errors, and should be used for saline solutions only when absolutely necessary, and then with an equivalent amount of salt added to the standards.

Lepper and Martin [30] showed that phenol red in a phosphate buffer has no salt error if the concentrations of sodium and phosphate ions are equal. If the former is higher, the colorimetric pH values are high, and *vice versâ*. With reference to the effects of different salts Michaelis and Gyemant [31] found that divalent anions produce a greater salt error than divalent cations, and both produce greater errors than monovalent ions.

In doubtful cases the behaviour of the indicator may be checked by the use of another indicator covering the same range, or if this is not possible, by the electrometric method. In this connection it should be borne in mind that other substances may react in specific ways with certain indicators, *e.g.*, phthalate buffers precipitate methyl violet, though the 0·2*M* solutions suggested (p. 22) are sufficiently dilute to be harmless. With solutions of unknown composition it is necessary to make assumptions as to the amount of salt present, but any error involved should not be large.[32]

The Protein and Colloid Errors.—Proteins are often encountered in solutions of biological origin. Unfortunately, on account of their amphoteric nature they tend to combine with both acids and bases, and for this reason may interfere with colorimetric measurements, particularly when azo dyes are used. The magnitude of the error for a typical protein may be gauged from the corrections given in Table 6 (p. 146). They

are usually small for indicators of simple constitution (*e.g.*, the nitrophenols) and are smaller for the products of protein hydrolysis than for the proteins themselves, particularly if the latter are complex and present in high concentration. Proteins which tend to pass into the colloidal state may even remove indicators from solution by adsorption, and so decrease the intensity of the colour.

Lepper and Martin [33] showed that up to 7 per cent. of pure egg-albumin produces no error with neutral red or phenol red. Gutbier and Brintzinger,[34] who established the same fact for gelatin, gum arabic, and dextrin, also showed that colloids may depress the $H^{\cdot}$ and OH' ion concentrations in acid and alkaline solutions respectively.

The same directions for the elimination of these errors apply as in the case of the salt error, *i.e.*, a known correction should be applied, or the method standardised electrometrically or in the presence of known amounts of protein. Tests with several indicators of widely different compositions are also useful.

Temperature.—In general it is not necessary to measure pH values at temperatures other than 15 to 27° C., and the temperature corrections shown in Table 6 (p. 146) are therefore seldom required. This table may, however, prove useful when solutions which are liquid only outside this range are being examined, or when for other reasons very high or low temperatures are to be used. Indicators which are weak acids are least susceptible to high temperatures.[35] If necessary, comparison may be made with a standard solution at the same temperature.

Coloured Liquids.—There are several methods for the elimination of the natural colour of a solution. Indicator papers and the method in which a compensating tube or test solution is placed in the colorimeter behind the standard have already been discussed (p. 91). Alternatively the colour of the solution may be imitated by adding to the standard the required amount of a 0·01 to 0·02 per cent. solution of appropriate colour selected from the following (Sörensen [36]) :—Bismarck brown, curcumine, methylene blue, helianthin, tropaeolin, safranine. Approximate results are obtained by mixing a drop of solution and indicator on a white opal tile and comparing the colour with that produced with a drop of buffer solution treated similarly.[36]

The procedure in which the colour is reduced by dilution of the solution is not to be recommended unless it is certain that the solution is sufficiently well-buffered to resist any pH change when diluted to twice its volume. The so-called "dilution method" described by Atkins and Thompson [37] is also suitable for coloured or turbid solutions, the test solution being diluted

(*e.g.*, in powers of 2) to 2, 4, 8, 16, and 32 times the original volume, and the pH determined colorimetrically on those dilutions which are sufficiently colourless. These values are plotted against the logarithm of the dilution (log $1/C$) and the straight-line graph extrapolated to zero dilution (*i.e.*, to the concentration of the original solution) and the corresponding pH thus found.

The success of this method depends on a straight-line graph being obtained, and if certain assumptions are made, which do not, however, affect the case in point, it can be shown theoretically that this condition is normally satisfied. Thus, for strong acids C_{H^+} will be almost equal to the concentration (C) or normality, and $pH = -\log C_{H^+} = -\log C$, which is the equation of a straight line. Similarly, for a weak acid $(C_{H^+})^2 = K \cdot C$, whence $pH = -\log C_{H^+} = -\frac{1}{2} \log K - \frac{1}{2} \log C$, and since K is constant this is also a straight line. Similarly, for buffers, $pH = pK - \log (C - C_B)/C_A$.

The effect of colour (or turbidity) is also reduced by the use of methods in which the solution is viewed in a thin film (*e.g.*, the capillator method, p. 93), and the writer has used successfully a thin layer of coloured liquid held between two thin glass plates separated by a strip of glass 1 mm. thick. The disadvantage of such methods is that disproportionately large amounts of indicator must be used to produce the required intensity of colour, especially as errors due to colour are most pronounced at pH values for which the best indicators are those yellow in colour.

Turbidity.—So long as the source of turbidity does not tend to remove the indicator by adsorption its effect may be eliminated by some such method as described for coloured solutions. A 0·1*N* suspension of pure barium sulphate in water will be found useful for the purpose of imitating turbidity in a test solution. With badly-buffered solutions the buffer and indicator may be added to the test solution itself, and the mixture used as a standard. Filtration should, as far as possible, be avoided, as changes in pH of as much as 0·5 have been shown to be produced in some cases by this operation, probably on account of the adsorbtive nature of the filter paper.

Weakly-Buffered Solutions.—The pH value of such solutions may be influenced by the acidic or basic nature of the added indicator if this is not accurately neutralised as described on p. 87. Oeman [38] overcomes this difficulty by plotting the observed pH value against the number of drops of indicator added, and extrapolating the curve backwards to a zero concentration of indicator. Prolonged contact with air or even with glass may also produce an error, and determinations should be carried out as rapidly as possible.

Miscellaneous Sources of Error [39].—Specific ions, immiscible or mixed solvents, or solvents other than water, may also affect the results. Indicators may be precipitated out of solution on standing, or they may be destroyed by bacterial action. Indicators that behave as acids and bases are usually more and less sensitive to hydrogen ions, respectively, in the presence of alcohol. Ionisation is, in fact, always less in the presence of non-aqueous solvents than in water. Reaction between indicator buffers has also been known to occur (p. 98). It has been stated by Eisenbrand [39] that the effect of the presence of the indicator itself can only be eliminated completely when its concentration in the liquid is less than 10^{-14} grm.-mol. per litre. This means, however, that only fluorescent indicators can be used to give results with a high degree of accuracy.

These miscellaneous sources of error usually arise in particular cases, and it is not possible to suggest a procedure to cover them all. A method may always be standardised by the addition of the interfering substance to the standard, and there is always a final appeal in the electrometric method. Errors due to technique such as the amount of indicator used, the thickness of the layer taken for the comparison, lack of uniformity of the containing tubes, etc., have already been dealt with.

Finally, it should not be imagined that the method is beset with sources of error since those described are found only in relatively rare cases, and are easily detected and easily eliminated.

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PART IV

METHODS AND TECHNIQUE APPLICABLE TO PARTICULAR CASES

It will be understood that the methods and technique described above are of a general character only, and that in the applications of pH determinations in industry, situations frequently arise which require special treatment. Sometimes, for instance, it is necessary to modify the apparatus to exclude air, or in other cases the experience of previous workers is of value to determine which of the colorimetric and electrometric methods gives the more satisfactory results. The question of how to apply the colorimetric method to coloured solutions is one which is frequently met, though since liquids occurring in industrial processes are usually well-buffered, dilution may be used in most cases.

It is hoped, therefore, that the following pages which contain notes on the method and technique appropriate to a large number of particular cases, will prove useful when the methods already described give unreliable or even doubtful results. No attempt is made to discuss the rôle of hydrogen ion concentration as such in these cases, as such discussion is outside the scope of this book.

Agriculture

The influence of hydrogen ion concentration in soil science is of the greatest importance, since excessive acidity or alkalinity may readily produce infertility towards a particular crop, and even small changes in pH value may have far-reaching effects in particular cases.

Soil Acidity.—Soil is essentially a solid, though moist substance, and its pH value depends on the salts it contains. The principal problem in the determination of pH values is therefore to obtain a solution truly representative of the composition of the sample. Soils are well buffered,[1] and their pH values range from about 4 to 8·5. Acidity may be due to carbon dioxide, humus, clay and hydrolysed salts, whilst lime is the principal source of alkalinity. Calcium carbonate and clay are good buffers for the acids, whilst humus serves to buffer the bases. According to Goy, Müller, and Roos[2] soil acidity is characterised

by (1) total acidity as obtained by electrometric titration (see p. 107) with standard alkali solution to neutrality (pH 7·0); (2) exchange acidity, in which titration is carried to pH 5·0; (3) pH value; (4) buffer values (*a*) at pH 5, (*b*) at pH 6 (residual or hydrolytic acidity), and (*c*) at pH 7 (maximum value).

Sampling.—Fromageot [3] has pointed out that on account of the action of air and the slow rate of downward diffusion through soil, there may be considerable differences in pH value between the surface soil and that 7 inches below. Allowance should be made accordingly, and the sample taken by the usual method from the particular stratum required. Soils lose carbon dioxide and increase in pH value if dried in air, though Arnd and Siemens [4] remove this gas in a current of air from soils whose pH is more than 5, or in hydrogen if the pH is between 5 and 8·5. The effect of drying is most marked at high temperatures, and heavy soils, loams, and sands show it in decreasing order. It is better, however, to break up the soil in the usual way and to determine its pH value at once so that drying is unnecessary.[5]

Preparation of the Soil Extract.[6]—Opinions differ widely as to the best method. Some workers suspend the soil in water or in potassium chloride solution and take the pH of the suspension. This is impracticable when a colorimetric method is used, and, indeed, the small colloidal particles have been known to affect the hydrogen and even the quinhydrone electrode. Filtration [7] is certainly out of the question even if extracted papers are used and the first runnings rejected, as it raises both the pH value and buffering power (see p. 133). Dialysis [8] is not advisable for the same reason, and because it is too lengthy, though the percolator or centrifuge may often be used with advantage.

Perhaps the most reproducible values are obtained by shaking the soil for a few seconds with an equal volume of distilled water and testing the top layer after the sediment has been allowed to settle for 30 secs. In certain cases a soil/water ratio of $\frac{1}{2}$ or $\frac{1}{4}$, and a longer extraction period (10 mins.) has been found necessary,[9] but it should be remembered that equilibrium between the soil and water is attained relatively slowly, and that it is better to stop the extraction after a definite period than to incur the risk of the other errors involved by prolonged waiting till it is complete. Some soils, especially those poorly buffered, attain equilibrium more rapidly than others (*e.g.*, suspensions of air-dried soils should be kept for 20 hrs. to peptise the clay completely), so that the conditions of extraction may be varied slightly according to the circumstances without appreciable error, so long as they are maintained constant in comparative experiments.

Methods.—The Clark rocking electrode [10] (p. 44) was

formerly the type of hydrogen electrode considered most suitable for the measurement,[4] but it is, of course, subject to disadvantages common to most hydrogen electrodes, and where an electrometric method is desired it has been replaced principally by Bijlmann's quinhydrone electrode.[10] A hydrogen electrode vessel for those who prefer to use unfiltered soil suspensions has been suggested by Bray.[11] It consists of a Gooch crucible or funnel in which 10 grms. of soil and 25 c.c. of water are placed, while the hydrogen is bubbled upwards through the stem of the funnel and keeps the solid in suspension. The electrode and connecting tube dip just below the surface of the liquid, and should not touch the suspended particles.

Comparison of the hydrogen and quinhydrone electrodes[9, 7] has shown that the latter may be used with confidence up to pH 8. For some soils, antimony or gold[12] may be found preferable to platinum as an electrode material, and in the former case $pH = 2{\cdot}04E - 0{\cdot}469$. Readings should normally be taken at minute intervals after immersion of the electrode until a constant value is obtained, though in the case of suspensions it is advisable to fix this immersion period (say 15 mins.) in advance and to keep the suspension well stirred. The quinhydrone electrode gives high results with soils containing relatively large quantities of manganese,[13] and the presence of hydrogen sulphide is, of course, also likely to foul the electrode.

In many cases, especially field work, a high degree of accuracy is not required, and the colorimetric method is by far the more convenient. Olsen and Linderström-Lang[14] tested nearly 100 soils by the quinhydrone and (Clark and Lubs) colorimetric methods, and concluded that in some cases the former may be as much as 0·8 pH high. The colorimetric method gave slightly high results between pH 5·5 and 7·0, the buffer range of carbon dioxide, and slightly low results outside this range. The error, however, changes regularly with pH value, so that if a correction curve is plotted, the pH may be determined with an accuracy of 0·15 pH, which is usually ample. Gadd's[15] method is ingenious if not very exact. The colour of 5 c.c. of soil extract (1 : 2), which need not be filtered, and to which 0·6 c.c. of indicator-solution is added, is compared with the colours of similar mixtures of extract and indicator with 10 drops of buffer solution. The pH of the latter buffer is varied until no colour change is produced on its addition, and the pH of the buffer is then that of the soil.

Lime Requirements.—Hardy and Lewis[16] claim to have obtained rapidly results which represent closely the true lime requirement of the soil, as follows. The finely-divided soil is shaken with 4 parts of 0·2*N* calcium chloride solution, the pH

taken with the quinhydrone electrode, and 5 c.c. portions of 0·03*N* lime-water added, shaken for 3 mins. and the pH taken. When pH 7·5 is reached, the results are plotted and the amount of lime to give pH 7·0 is found. To determine complete saturation a final pH of 8·5 has been recommended.[17]

A convenient field apparatus for sorting purposes (specially recommended for golf links), made by the British Drug Houses, Ltd.,[18] is a small white porcelain boat with two compartments of unequal size connected by a narrow channel. The larger is three-quarters filled with soil, a special mixed indicator added drop by drop until the soil is well wetted, and the excess then drained into the smaller compartment. A full red-colour indicates a very acid soil (pH 4·0 or less), orange pH 5·5, yellow pH 6·0, green pH 7·0 (neutral soil), and blue pH 8·0. The indicators brom cresol green, brom cresol purple, brom thymol blue, and phenol red cover the same range (pH 3·6–8·4) very satisfactorily. The Capillator (p. 93) made by the same firm may also be used in conjunction with the above boat if higher accuracy is required, and in this case equal volumes of distilled water and soil are used. If necessary the colour compensation cell is used, or the decanted aqueous extract may be cleared completely by transferring it to a porcelain boat coated with paraffin wax, from which it may be drawn off clear after a minute or so.

Mention may also be made of a very rough but easily applied test for lime requirement described by Comber.[18] The fairly dry soil is shaken in a test-tube with a saturated solution of potassium thiocyanate in alcohol. The intensity of the red colour obtained after 30 mins. is an indication of the lime requirement of the soil, and a pale colour or absence of colour means that the soil is sufficiently alkaline. This colour depends on the formation of the red compound ferric thiocyanate from the reagent and the iron in the soil, the iron being dissolved out of the soil to greater extents by solutions of greater acidities (lower pH).

The same writer points out that these tests are particularly valuable if considered in conjunction with field symptoms of lime shortage, *e.g.*, sudden failure of acid-sensitive crops such as barley and sugar beet. Spurrey and mayweed are often found on acid arable land, and bent-grass, sorrel, and woodrush on acid grassland. Sectional examination of the soil is advocated to avoid unnecessary liming where this is not really required.

Analysis

Complete volumes could be, and have been,[19] devoted to the uses of pH determinations in analysis. All that falls within our present scope is to give an account of some underlying principles

and of a few useful and typical methods, and to indicate the literature in which further information may be found.

Electrometric Titration.—If a certain volume of acid is titrated with a standard solution of an alkali without addition of an indicator, the course of the neutralisation reaction may be followed from the shape of the curve obtained when the amount of alkali added (or proportion of acid neutralised) is plotted as abscissa and the pH of the mixture (or *E.M.F.* of the cell) as ordinate. In normal cases a steep portion of the curve appears at the pH corresponding with each ionisation constant of the acid, and as shown on p. 15, the actual position of the steep portion depends on the strengths of the acid and base concerned. This supplies an obvious means not only of investigating the properties of acids and bases, but also of titrating them accurately or of adjusting the pH of a solution to a predetermined value.

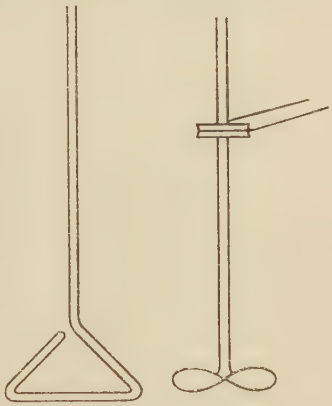

FIG. 33.

The only additions required to the apparatus already described are a burette and a stirrer. Where a vigorous stream of hydrogen bubbles through the solution the latter may not be necessary, but in any case it is easily constructed from a piece of glass rod suitably bent (Fig. 33), and it may be turned by means of a pulley-wheel driven from a small motor. The standard solution is added from a burette to the known volume of acid or alkali contained in a beaker, and the stirrer is kept working continuously. It will be found that in the early and final stages of titration addition of the reagent produces a relatively small change in pH, but that as the steep portion of the curve is reached the reverse occurs. The titration curve is complete when an excess of the added reagent is present such that the pH falls to about 1 (in the case of added acid) or rises to 13 (for added alkali). The exact neutral point is, of course, 7·0, but the end-point depends on the nature of the acid, and occurs where the potential changes most rapidly. Where the object of the titration is to determine salt formation, the flat portion of the curve is the end-point. Thus, in Fig. 34 the point A (pH 6·5) represents the formation of sodium bicarbonate and B (pH 10·2) that of ordinary sodium carbonate. The same results can, of course, be obtained by the choice of a suitable indicator changing at the desired pH, but the course of the reaction cannot

be followed, nor can the method be used in coloured solutions (*e.g.*, for dyes, p. 118), unless indirect means are employed (p. 99). As a matter of fact, these titration curves of acids and bases are an invaluable guide to the choice of a suitable indicator, especially where the acid or base is extremely weak (*e.g.*, sugars or glycerol).

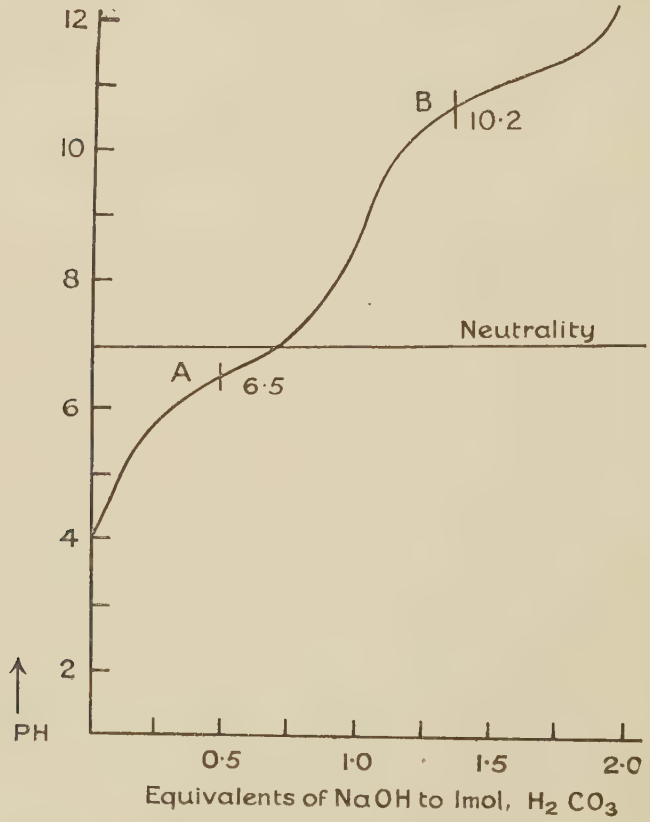

FIG. 34.

Reference may also be made here to the lists of acids and bases with their ionisation constants (p. 141), and to the neutralisation curve of phosphoric acid (p. 20).

The principles of electrometric titration are not confined to neutralisation reactions. Any reaction (*e.g.*, precipitation or oxidation-reduction reactions [42]) in which the end-point is distinguished by a relatively sharp change in potential may, in fact, be carried out

in this way, and the technique is similar in all cases except that the electrodes must often be modified to suit the particular case. *Conductometric titrations*,[19] in which the change in electrical conductivity of the solution is measured, are also now largely used for the same purposes, and should be distinguished from *potentiometric titrations*, in which the change in potential is measured and with which we are here concerned.

The following conditions are desirable for potentiometric titration :—

(1) Side reactions should be absent. (2) The relation of the reactants should be stoichiometric (*i.e.*, the products of reaction formed should be definite compounds, there should be no adsorption, etc.). (3) The reaction should proceed fairly rapidly, and as far as possible in one direction. (4) A suitable indicator electrode should be available. (5) There should be a marked change in potential at the end-point.

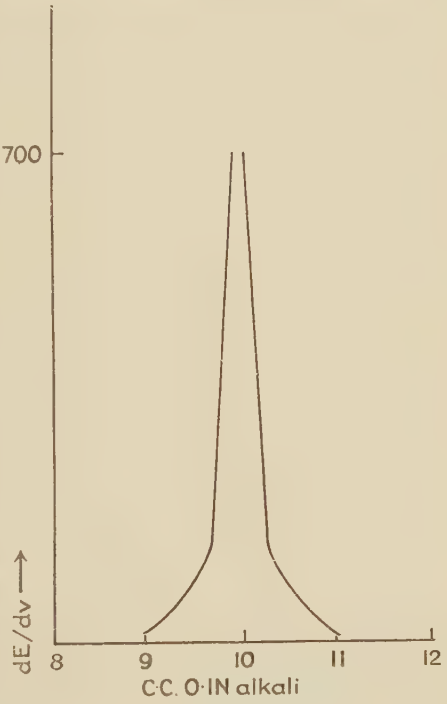

FIG. 35.

Practical Considerations.—Normally, the reagent is added in 1 to 5 c.c. portions until the end-point is approached, when smaller additions (0·1 c.c. or less) must be made. The readings are recorded after the stirring has had its effect, and should not alter before the next addition is made. Sometimes, however (*e.g.*, with beer worts and amino acids), different results are obtained according as acid is added in one large or in several small portions, and such cases are discussed on p. 121. The quinhydrone electrode is less susceptible than the hydrogen electrode to these effects. With phosphate buffers equilibrium is reached rapidly, whilst there is a lag of a few seconds with carbonate buffers.[20]

There are certain methods [21] by means of which the end-point of a potentiometric titration may be determined much more conveniently than by finding the mid-point of a rather ill-defined straight portion of a curve. Perhaps the best of these is to calculate for each addition of reagent the quantity dE/dv, which is the rate of change in *E.M.F.* compared with the volume (v) of solution added. It is calculated by dividing the number of millivolts rise or fall in *E.M.F.* by the number of c.c. of solution required to produce this change. A little consideration will show that dE/dv rises to a maximum value at the steep portion of the curve and then descends. The table shows an example (titration of 10 c.c. of 0·1*N* hydrochloric acid with 0·1*N* alkali), and Fig. 35 shows the type of curve obtained if dE/dv is plotted against the volume of reagent added. It is not necessary, however, to draw a curve in such cases.

Total Volume (v) of 0·1*N* NaOH added.	Change in v (dv).	*E.M.F.* volts.	Change in *E.M.F.* (dE) volts.	dE/dv.
c.c.	c.c.			
0	—	0·530	—	—
5·00	5·00	0·530	0	0
7·00	2·00	0·530	0	0
8·00	1·00	0·530	0	0
9·00	1·00	0·531	1	1
9·50	0·50	0·535	4	8
9·70	0·20	0·539	4	20
9·80	0·10	0·547	8	80
9·90	0·10	0·556	9	90
10·00	0·10	0·576	20	200
10·05	0·05	0·661	85	1700
10·10	0·05	0·721	60	1200
10·20	0·10	0·766	45	450
10·50	0·30	0·787	21	70
11·00	0·50	0·812	25	50

The reagent should be added as far as possible in equal but not too small amounts in the neighbourhood of the end-point,[22] and the potentials measured on each side of it.

The quinhydrone electrode is well-suited for potentiometric titrations and is often used, and in many cases an ordinary piece of bright platinum wire may be immersed in the solution and used directly without even introducing hydrogen. This, of course, only applies when the change in potential at a particular end-point is to be indicated, and should not be used without standardisation for the determination of actual potentials or of pH values. A useful arrangement, where one solution only is being

used continually, is that proposed by Willard and Boldyreff [23] (Fig. 36), in which the platinum electrode is sealed into the jet of the burette itself.

A further advantage of the fundamental principle that potentiometric titrations are concerned with changes in potential and not with absolute values, is the fact that the use of a potentiometer may be avoided. Pinkhof,[19] for example, determined the potential of the end-point of a particular reaction by mixing carefully-measured quantities of reagent. Now, it follows that since the end-point of a particular reaction is always the same, the potential between a mixture of reagents at the end-point and the solution being titrated will be zero when they are both the same, *i.e.*, when the end-point is reached in the latter. Pinkhof's system is, therefore, electrode | mixture of reagents at end-point | liquid connecting bridge | solution to be titrated | electrode. If the two electrodes are similar, the potential of this cell will fall to zero when the end-point is reached. The obvious drawbacks are the preliminary titration to find the end-point, and the fact that each titration requires its particular electrode system. Also, there is no warning of the end-point or means of compensating for differences in temperature, time-effect, or presence of other substances in the reaction mixture. The method, however, is rapid and has many advantages in routine work, where end-point solutions may be made up in advance for every type of titration required.

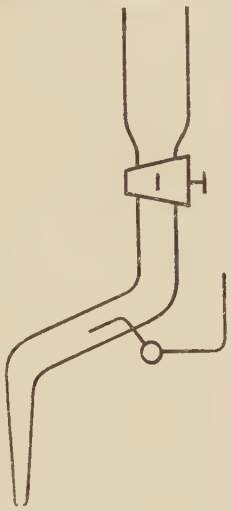

FIG. 36.

Differential Titration [24].—This method may be used for neutralisation reactions, and once the technique has been mastered gives accurate results without the use of standard electrodes or titration curves. Two similar electrodes are placed in separate portions of the test-solution which are connected by a liquid bridge to give the system, Pt | solution | bridge | solution | Pt, and the two portions of the liquid titrated at different rates. The *E.M.F.* of this cell is due to the difference in concentration between the liquids immediately surrounding the electrodes in the two cases, and is a maximum at the end-point. McInnes and Dole [25] have described a simple apparatus.

Colorimetric Titration.—Kolbach [26] has also adapted colorimetric methods to acidity determinations of liquids (*e.g.*, wort and beer) which may change in colour, turbidity, salt or protein

effects during titration. A buffer solution having the pH of the desired end-point is diluted to three times its volume and 20 c.c. of sample added, with the indicator, to 10 c.c. Standard acid or alkali is then added to a mixture of 20 c.c. of sample and 10 c.c. of water and indicator until a colour match is obtained. An equal volume of acid or alkali, plus 10 per cent., is then added to the buffered portion, a match again obtained and an equal volume of reagent added also to a fresh buffer-sample-indicator mixture. The buffer has now been diluted with sample having its own pH, so that its pH is unchanged, and a fresh 20 c.c. of sample and 10 c.c. of water (with indicator) may now be titrated to a colour match.

The course of titration may also be followed by colorimetric determinations of the pH values after each addition of reagent, but the method is too cumbersome to be of great use. Alternatively the colorimetric method in which a selenium cell is used (p. 96) may be adapted in the same way.[19, 29] In this case, the change in colour of the indicator shuts off the light falling on the light-sensitive cell and a current controlled by a thermionic valve then actuates the relay which turns off the burette-tap. Good results are obtained with one-colour indicators, but for others suitable screens must be provided. Though the method is in its infancy it shows great promise and special light-sensitive cells have been constructed for the purpose. Fluorescent indicators [27, 28] (*e.g.*, iodo-eosin) are highly sensitive even in very dilute solutions (0·001*N*) of acids and bases.

Automatic Electrometric Titration [29, 30] is based on the same principles as those already described in the preceding paragraph and in connection with the automatic determination of pH values (p. 96). The only addition to the apparatus is an electric relay controlling the tap of a burette and set in action when the pointer of the galvanometer reaches a certain point corresponding with a predetermined pH value.

Weak Acids and Bases [31, 85].—Weak acids and bases, which cannot be titrated by the ordinary method, may be determined if their ionisation-constants are known. Thus, Harris [32] has devised methods similar to those of Michaelis and Rona,[33] and of Tague,[34] for the calculation of the ionisation constants of acids and bases which form salts readily hydrolysed in solution. If we take a weak acid as an example, we know (p. 16) that if the degree of ionisation is small, $K_{acid}=C_{H^\cdot} \cdot C_{salt}/C_{acid}$, and a certain amount of the added base will fail to react. This quantity, however, will determine the pH value ($C_{H^\cdot}$) and C_{salt} may therefore be calculated from $C_{H^\cdot}$ and the amount of alkali added. Hence, if K_{acid} is known for the pH concerned, the volume of base which failed to react may easily be obtained, and this

subtracted from the total volume added will give the amount used for neutralisation. For further details reference must be made to the original papers and to the table of ionisation-constants on p. 141.

The above method is particularly useful for *amino-acids*, *alkaloids*, and *ampholytes* in general. Indicator methods may, however, also be used, especially for alkaloids (p. 134), so long as the correct indicator, obtained by reference to the ionisation constant, is chosen. (See also Boric and Carbonic acids.)

Ammonia may be determined by back-titration by means of the quinone-quinhydrone electrode (p. 48), even if its pH value is greater than 7, by the procedure of Prideaux.[35] The method was applied to ammoniacal gas liquors, 20 c.c. of an approximately 0·1*N* solution of which were pipetted into an excess of 1·0*N* hydrochloric acid, boiled for an hour, if necessary, to expel volatile acids, mixed quinone and quinhydrone added, and the excess of acid titrated with 0·1*N* alkali. The potential of the theoretical end-point at 18°–25° is [(0·7044–0·251)+0·058 pH], and pH=4·685—0·5 log *c*, where *c* is the concentration of ammonium chloride produced. The results obtained are in good agreement with those found when methyl red is used, but, of course, they are independent of any colour already present in the solution. If an indicator is used, Bailey[35] prefers brom cresol green, and titrates to pH 5·1 for hydrochloric acid and 5·7 for sulphuric acid.

Boric Acid.—See *Foodstuffs* (Preservative).

Carbonic Acid, Carbonates, and Bicarbonates.—The equilibrium in solution of these three types of compounds is of great significance in Nature, since they form an important buffer system (see especially, *soils*, *blood*, *sea* and other *water*, *brewing*, etc., for the discussion in each case of their influence on the measurement of the pH value). Here, however, we are concerned with points of purely analytical interest and carbonic acid-carbonate equilibria are instructive as an illustration of the selective uses of indicators for the titration of weak or strong acids or bases.

Briefly, carbon dioxide dissolves in water to form the weakly-dissociated, dibasic carbonic acid, $CO_2+H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^{\cdot}+HCO_3' \rightleftharpoons 2H^{\cdot}+CO_3''$. When carbonic acid is titrated with a base, with phenolphthalein as indicator, an alkaline reaction is obtained only after neutralisation of both hydrogen atoms, since phenolphthalein is sensitive to weak acids forming easily-dissociated alkaline salts (*e.g.*, $Na_2CO_3+H_2O \rightleftharpoons NaOH+NaHCO_3$). Solutions of such soluble carbonates, therefore, are alkaline to phenolphthalein, whilst the partly neutralised carbonates (acid carbonates or bicarbonates, *e.g.*, $NaHCO_3$) give a red colour only

after the solution has been heated so as to produce the completely neutralised alkaline form. Methyl orange, on the other hand, changes colour at a distinctly acid pH value, and is, therefore, not sensitive to weak acids, though it responds to weak bases. It may accordingly be used for the direct titration of carbonates and bicarbonates with hydrochloric acid. The following methods of determination of carbonic acid distinguish between cases in which phenolphthalein or methyl orange are used as indicator (cf. boric acid, p. 126). It is interesting to note that except in the presence of carbon dioxide, methyl red is more sensitive than methyl orange. The latter should not, however, be used in hot or in alcoholic solutions.

(1) *As free carbonic acid* (H_2O+CO_2).—Add excess of standard baryta to fix the carbonic acid, and back-titrate the excess with 0·1*N* hydrochloric acid to phenolphthalein: $H_2O+CO_2+Ba(OH)_2=BaCO_3+2H_2O$.

(2) *As bicarbonate.*—Titrate directly with hydrochloric acid to methyl orange (sensitive to strong acids): $NaHCO_3+HCl=NaCl+H_2CO_3$. (Alternatively, remove the carbon dioxide by boiling with excess of standard acid, and determine what remains of the latter by back-titration with alkali, with litmus, or other appropriate indicator.)

(3) *As carbonate.*—Proceed as in (2), using methyl orange: $Na_2CO_3+2HCl=2NaCl+H_2CO_3$. The same alternative method may be used.

(4) *In presence of bicarbonate* (and absence of magnesium).—(*a*) Determine bicarbonate as in (2). (*b*) Add an excess of standard baryta in the presence of excess of barium chloride (to prevent formation of free alkali, thus, $NaHCO_3+Ba(OH)_2=BaCO_3+H_2O+NaOH$), and titrate the excess with hydrochloric acid to phenolphthalein. Then [baryta used for (*b*)—acid used for (*a*)] ×0·0022 =free H_2CO_3.

(5) *In presence of carbonate.*—$Na_2CO_3+H_2O+CO_2=2NaHCO_3$. (*a*) Total alkalinity is obtained by titration with standard acid to methyl orange. (*b*) Bicarbonate is obtained by the addition of an excess of 0·1*N* sodium hydroxide and neutral barium chloride solutions, and titration of the excess of alkali with 0·1*N* acid to phenolphthalein: $NaHCO_3+NaOH=Na_2CO_3+H_2O$, and $Na_2CO_3+2HCl=2NaCl+H_2O+CO_2$. The half-neutralisation point may be found by titration to a mixture of cresol red and thymol blue, and if brom phenol blue is then added, a sharp change from blue to green occurs on complete neutralisation.

For potentiometric titration of carbonic acid, see Fig. 34, p. 108.

Electro-deposition (see also p. 131), and **precipitation** methods of analysis are also dependent on the hydrogen ion concentration, but the extent of this dependence cannot be discussed here, nor

is any noteworthy modification in the methods of pH determination necessary in such cases. Colorimetric methods are quickest and usually sufficiently accurate where the pH has to be adjusted to obtain optimum conditions of precipitation or deposition.

In connection with *precipitation reactions*, however, it must be mentioned that Hildebrand [36] as long ago as 1913 used the hydrogen electrode to follow the changes in pH on precipitation of metallic hydroxides, and it was shown later, notably by Britton,[37] that there is a narrow pH range (Table 3, p. 144) for such precipitation depending on the nature of the precipitate. It thus became possible to control the separation of hydroxides by adjusting the pH to the optimum for precipitation (the iso-electric point). Both colorimetric and electrometric methods have been employed to measure this pH, and the oxygen electrode may replace the hydrogen electrode where the latter cannot be used, *e.g.*, in presence of copper salts (Ralston [38]), to follow the pH changes of a reaction. Metal electrodes are also used.[35, 40] It may also be mentioned as an example of a different type, that the titration of halogen salts with silver nitrate, with potassium chromate as indicator, may be carried out in a solution of any reaction so long as the pH is first brought between 5 and 7 by addition of a sodium acetate-acetic acid buffer.[39]

Biochemistry

The study of the measurement of hydrogen ion concentration probably owes its origin to biochemical research, and it is no exaggeration to say that the requirements of biochemical problems have, more than any others, led to improvements in technique. Although most biological fluids are well-buffered, they often change very rapidly in pH when removed from their natural environment, and this means that methods must be devised by means of which the pH may be determined rapidly either *in situ*, or else externally but in the absence of air. Often, also, only small quantities of sample are available, and several micro-methods, especially those in which a glass electrode is used, have therefore been suggested.[37, 41] Since biochemical liquids usually have a pH between 6 and 8, phenol red and brom thymol blue are the most useful indicators.

Mansfield Clark and his co-workers,[23, 42] have recently also investigated the relation between the electrode potentials induced by bacterial reduction and the pH value, and have examined the actions of a number of oxidation-reduction indicators.

A number of typical examples of biochemical interest follow in alphabetical order.

Amino-Acids.—The electrometric titration of ampholytes was discussed under the heading *Analysis*.[32] In the case of amino-acids the quinhydrone half-cell with a gold electrode has been found suitable for pH values up to 8. Indicator methods do not as a rule give good results in such cases, as the ionisation constants of the acids are usually too small. Glutamic and aspartic acids are exceptions. If, however, an excess of a neutralised solution of formaldehyde is added, the methylene-imino group replaces the amino-group thus, $R.NH_2+HCHO \rightarrow H_2O+R.N:CH_2$. Now Harris [32] has shown that the ionisation constants of these new compounds are about 1000 times higher than those of the corresponding amino-acid, so that they may be titrated with alkali in the presence of phenolphthalein. This is known as *formol titration* (Sörensen [43]).

Blood.—This is an instance of a very well-buffered, almost neutral fluid (pH 7·5 for venous blood and serum, and 7·8 for arterial blood), whose pH changes rapidly on exposure owing to loss of carbon dioxide. Whatever method is used, therefore, should be standardised before the experiment. A layer of pure paraffin wax is often employed to protect the blood from air, but this is not very practicable where the ordinary hydrogen electrode is used. If a collodion sac of constant permeability is obtainable, it is best to remove the electrolytes from the blood by dialysis through the sac into 0·85 per cent. carbon dioxide-free, salt solution, which is isotonic with the blood serum, and therefore introduces no osmotic pressure effect (p. 30). If the blood is diluted, say, 20 times with this salt solution, the coloured portion may be removed in the centrifuge, and an almost colourless liquid obtained which may be matched in a Duboscq or other colorimeter (Cullen [44]). Whether the blood should be diluted or not has been discussed by many workers. Sendroy and Hastings varied the concentrations of the acid and alkaline indicators, and they maintain that by working at 38° (body temperature) the dilution and temperature corrections cancel out. Otherwise, pH at 38°=pH at $t°+0·01\ (t-20°)-0·22$. This method gives fairly reliable results, but has been attacked by other workers.[44, 45, 47]

As for the indicator, the one-colour type (*e.g.*, a 1 per cent. solution of *p*-nitrophenol) which show a progressively increasing intensity of colour is preferable to those in which a change of colour is produced. Cloudiness may be compensated by baryta placed in the standard.[45]

Of the *electrometric methods*, the glass electrode will be found particularly suitable for blood. The quinhydrone electrode has, however, also been used with success in blood diluted with 3 vols. of water. Liu [46] records a sharp rise in *E.M.F.* in such cases

to a maximum value which gives a pH slightly higher than that obtained with the hydrogen electrode, followed by a slow fall. This may be due to reduction reactions between the quinhydrone, hydrogen ions, and the hæmoglobin.

Where the hydrogen electrode only is available, some special form has to be devised to overcome the difficulty of bubbling gas through the blood. Syngedaw [47] has described a permanently-saturated type in which the bubbler (A) is so close to the electrode (B) that there is always a drop of liquid connecting them which keeps the electrode saturated and blocks up the outlet when the gas is cut off (Fig. 37). The blood is supplied to the electrode and drawn into A at the rate of about 1 drop per min., and at the same time a slight pressure from a mixture of hydrogen and carbon dioxide is applied to the drop through A, the excess of which escapes in small bubbles through the drop. The electrode should be washed with an isotonic solution of pH 7·5.

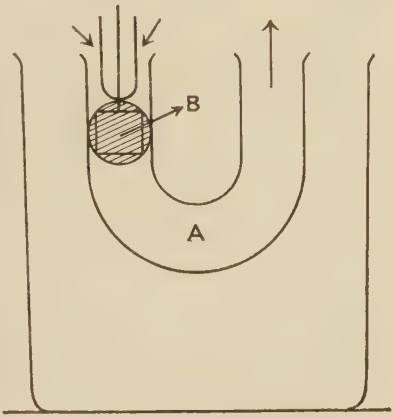

FIG. 37.

Enzymes.—Recent work [48] has shown that one of the principal factors influencing enzyme reaction is the pH of the medium. Certain enzymes react only within narrow pH limits, and colorimetric methods are usually employed to facilitate the adjustment of the pH of the medium. An article by the writer on this subject [48] contains a full discussion of the pH values required by most of the common enzymes, and of the means employed to obtain them. Fig. 2 on p. 12 includes the optimum pH range of a number of common enzymes. It should be remembered, however, that enzymes from different sources which bear the same name and act similarly on the same substrate may have different optimum pH values.

Nutrient Media [48].—Just as enzymes have optimum pH ranges, so also have organisms, and in the preparation of nutrient media this point has to be remembered. Formerly, comparative experiments in a particular medium were rendered possible by addition of a definite excess of alkali, though what was actually, if unconsciously, done, was to adjust the pH value.

Acid or alkali is added to the medium till an indicator mixed with a small portion of it attains a colour corresponding with the

pH required. Here again the colorimetric method is almost always used, as nutrient media are well-buffered and usually almost colourless, and a high degree of accuracy is seldom required. Thus, phenol red is used in the differentiation of typhoid and paratyphoid baccilli.

PH adjustments are of particular importance in the preparation of artificial media from phosphates and amino-acids, etc. Foreman and Smith [48] found that phosphates and creatinine exert their buffer effects in media at pH 7·2–6·3 and 5·0–4·5 respectively, and that other constituents (*e.g.*, amino acids, inorganic salts, etc.) accounted for only 10–15 per cent. of the titration value to methyl orange. The relation of pH and titratable acidity was studied for the various constituents, and it was concluded that $H^{\cdot}$ and OH' ions might exert a " depressor " effect independently of their effect on the reaction. The buffer effect at a particular pH value is found from the titration curve.

Saliva—Gastric Juices [12, 48].—Healthy saliva is normally slightly alkaline to litmus, but may vary between pH 5 and 7. Gastric juice has pH 5 and pancreatic juice pH 8·3. The electrometric method, particularly with Syngedaw's electrode [47] (p. 117) or with the quinhydrone electrode, is suitable for pH determinations, but the colorimetric method may give uncertain results. The relation of pH and acid taste is discussed on p. 25.

Skin.—The pH of skin, which is normally 4–8, is demonstrated by direct application of a moist indicator. In cases of eczema the skin may be even more acid than pH 4. Okunev [49] has used a quinhydrone electrode for tissues.

Urine [50, 51, 52].—In general, the problems arising are similar to those for blood. The approximate pH may be found colorimetrically after decolorisation of the urine with pure medicinal carbon as suggested by Silberstein.[50] The carbon, however, may adsorb $H^{\cdot}$ and OH' ions, and for more accurate work the urine is diluted under a layer of oil with 5 parts of 0·9 per cent. sodium chloride solution as described under blood (Cullen's method,[44] p. 116). Then pH at 25°—0·2=pH at 38° of the undiluted urine. A gold quinhydrone electrode has proved suitable for the electrometric method and may be used for the titration of organic acids.[51] Urine varies in pH between 5 and 7·5, and samples from the same source should normally show little diurnal variation.[52]

Dyestuffs

Callan and Horrobin [19] have applied potentiometric methods to the examination of dyestuffs, where colorimetric methods are, of course, impossible.

Sodium carbonate cannot be determined directly by the

quinhydrone electrode on account of the alkalinity of the solution, but a known excess of standard acid may be added, the carbon dioxide boiled off and the cooled solution titrated with standard alkali after addition of 0·5 grm. of quinhydrone. Since many dyes are themselves salts of organic acids the end-point potential of the electrode is affected, and it is therefore necessary to use an " end-point solution " of the necessary composition in the manner described on p. 111.

Acidity is important, especially when the dyestuff is a hydrochloride or sulphate of a colour base, and is determined by direct titration of a 0·5 per cent. solution with 0·1*N* sodium hydroxide solution in the presence of the quinhydrone electrode. Again, a buffered end-point solution of pH 5·9 may be used.

These authors have also applied potentiometric (and conductometric) titrations to oxidation-reduction reactions related to dyestuffs' practice, and to the determination of chlorides and sulphates in dyes.

The process of dyeing is actually an adsorption phenomenon and is therefore dependent on the pH value. For example, Thils [53] found that at pH 4·0 clays used for " filling " purposes have their maximum affinity for dyes.

Fermentation and Allied Industries

Bakery—Flour [58].—The pH of flour is determined by extracting the sample with water, when the proteins and phosphates, the principal buffers, are removed, to give a liquid of about pH 6 to 6·5. Bailey and Peterson [54] took one part of flour and five of water, and found that between 0° and 60° the temperature and period of extraction (1–6 hrs.) had no effect on the pH. Kent-Jones [55] showed, moreover, that the proportion of flour to water is also immaterial, and that the pH of the filtered extract is the same as that of the unfiltered suspension. He gives the following figures : commercial patent 5·90, commercial bakers' straight run 6·20, English straight run 6·28, low grade commercial 6·50. These and other results show that the best grades of flour have the lowest pH values, probably on account of their lower ash-contents.

Halton and Fisher,[56, 58] however, found that filtered extracts had a slightly lower pH, that the pH increases slightly with increase in the relative proportion of flour to water used, and also with the duration of the extract.

The large and variable protein content of flour introduces a correspondingly important protein-error into the colorimetric pH determination and a standardised method is therefore essential if the results of different workers are to be compared. At pH

6·0 electrometric and colorimetric methods are in agreement, but at pH 5·5 the latter gives slightly higher results, whilst at pH 5·0 the difference may amount to 0·15 pH (Kent-Jones). Methyl red, which has a low protein error, is therefore suitable in such cases. The procedure suggested by Kent-Jones [55] is usually followed in this country.

(1) Acidity due to potassium dihydrogen phosphate (KH_2PO_4) is found by titration with 0·05*N* sodium hydroxide solution in the presence of phenolphthalein (1 c.c.≡0·0068 grm.).

(2) Alkalinity due to potassium monohydrogen phosphate (K_2HPO_4) is found by titration with 0·05*N* sulphuric acid in the presence of methyl orange (1 c.c.≡0·00435 grm.).

(3) The pH value is measured. (*a*) *Colorimetric.*—A bright extract is obtained by shaking 10 grms. of flour, 100 c.c. of carbon dioxide-free distilled water, and 2 c.c. of toluene for 10 mins., and the suspension filtered after 35 mins. through a No. 5 Whatman paper. Methyl red (or phenol red) is used as indicator. (*b*) *Electrometric.*—A quinhydrone electrode is placed in the above flour extract, and linked up in the usual way with a similar electrode in a buffer solution of pH 3·6. Then, if *E* is the *E.M.F.* of the system in millivolts, pH=3·6+*E*/58·1. For the electrometric method a centrifuged or decanted extract may also be used, and gold may replace platinum as electrode material.

(4) The buffer action is expressed by ten times the decrease in pH value after addition of 10 c.c. of 0·01*N* lactic acid to 100 c.c. of extract. Electrometric titration of the extract with 0·02*N* acid or alkali also furnishes valuable information.

The American Association of Cereal Chemists [57] recommends a similar procedure which is also applicable to **bread, wheat,** etc., and other **cereals** and **cereal products.** (1) *Acidity.*—18 grms. of sample are shaken with 200 c.c. of boiled water for 10 mins. at 40°, filtered after 1 hr., and the last 100 c.c. collected and titrated with 0·05*N* sodium hydroxide solution to phenolphthalein (1 c.c.≡0·005 grm. lactic acid). *Pʜ Value.*—10 grms. are shaken with 100 c.c. of water at 25° for 30 mins., the liquid decanted and centrifuged after a further 10 mins., and then filtered. *Buffer Value.*—0, 0·5, 1·0, 1·5, and 2·0 c.c. portions of 0·1*N* lactic acid are shaken with a suspension of 10 grms. of cereal in 100 c.c. of water and 0·5 c.c. of neutral toluene for 1 hr. at 25°, centrifuged, filtered, and the pH of the extract plotted against the amount of lactic acid added. The buffer value is that volume of lactic acid which produces a pH of 5·0 in the original suspension.

Whittier and Grewe [58] applied Watson's method (p. 127) to flour, bread, etc., and found that reliable comparative results were obtained. The sample is made into a stiff dough with

quinhydrone and water, pressed round the electrode, and the reading taken after an hour.

Brewing.—Recent work, particularly that of Hagues,[59] has shown that useful information may be obtained from a knowledge of the pH of the brewing liquor, of the wort, and of the finished beer at racking. The early work of Parsons [60] indicated that for the brewing methods adopted in this country, the pH is about 5·2, 5·0, and 4·0 in the mash tun, copper, and fermenting-vat respectively. English two-rowed malts have pH 5·5, foreign six-rowed 5·7, chocolate 4·1, and brown malts 5·2. Each ingredient of beer (water, malt, hops, yeast, etc.) has a contributory effect on the pH of the liquor at each stage.

The determination of the pH value of the *supply water* or *mash liquor* presents no difficulties, and is usually made colorimetrically, but reference may also be made to the section on water in general (p. 134). Supply water is nowadays often treated for mashing purposes. Sometimes salts (*e.g.*, kainit or gypsum) are added, and sometimes the water is acidified with lactic or another acid to bring the reaction of the water to that at which the mashing proceeds to the best advantage. The pH may therefore vary from about 5 to 8, though the modern tendency is towards a distinctly acid liquor. These points must be taken into account when the method of determination or indicator is chosen.

The pH of the *wort* [61] will depend on the pH values of the mashing liquor, and of the constituents of the malt extracted during the mashing process. Its value is important since on it depends the "break" in the copper (pH 5–5·5), the antiseptic value of the hops (pH 5–7), and the rate of fermentation (pH 3·9–4·5). Wort is a coloured liquid, but since it is well-buffered, principally by phosphates and amino-acids extracted from the malt, it may safely be diluted several times, and the colorimetric method used. At pH 4·27 the salt error of an acetate buffer balances the dilution error of the wort. The quinhydrone electrode is equally useful, since the frothy and colloidal nature of the liquid renders the hydrogen electrode unsuitable.

It is obviously essential for a complete knowledge of the properties of a wort to know its buffering power, and this is determined by electrometric titration. Fig. 38 is taken from a paper by Hagues,[59] and shows the buffer curves of beer (A) and 100 c.c. of wort of pH 5·2 (B). *N* hydrochloric acid and *N* sodium hydroxide solutions were used for the titrations.

Hopkins and Kelly [62] found that different values of the pH of wort are obtained according as the acid is added in one large or in several small portions. Thus a pH of 6·0 dropped to 5·5 on addition of 10 c.c. of acid, but dropped far more after addition of five 2 c.c.

portions. It is considered that this is due to titration, in the latter case, through the iso-electric zone (see p. 115) of one or more of the nitrogenous wort-colloids, and that the amount of precipitate thus formed does not have time to combine with the small subsequent additions of acid. As far as possible, therefore, the acid should be added in one large portion to avoid this zone, especially when the

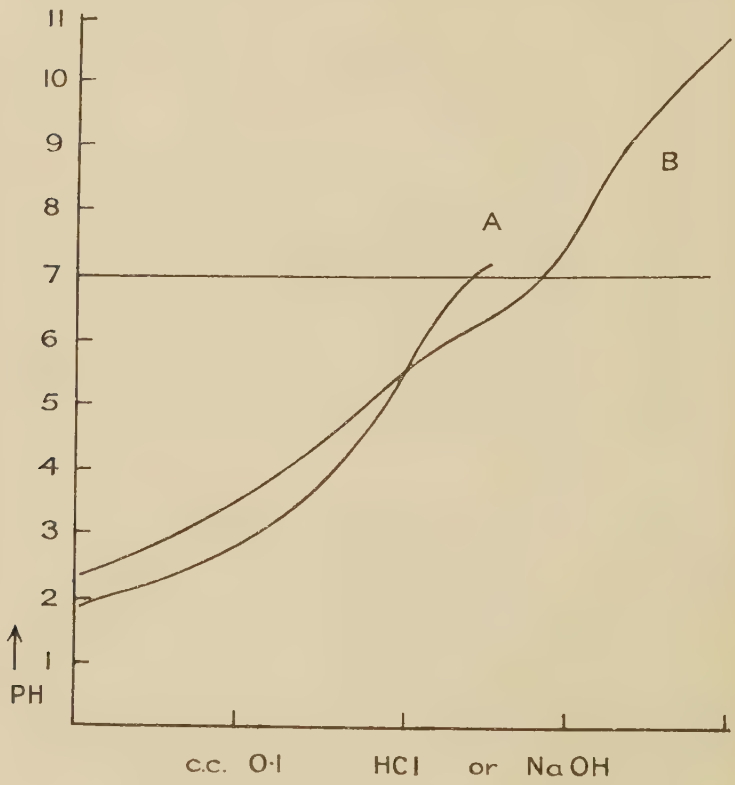

Fig. 38.

quinhydrone electrode is used. The hydrogen electrode probably promotes stirring, and the effect is more marked.

The same workers take the range pH 5·7–7·0 of the titration curve of wort to correspond with inorganic phosphate buffers, and pH 3·7–5·7 with amino acids and peptones. Of the latter, those corresponding with the range pH 3·7–4·3 are responsible for the subsequent stability of the beer. The buffer index (p. 21)

at about pH 4·4 indicates only free amino groups, and is independent of the effects of phosphates. Kolbach's method for the titration of beer may also be applied to wort (see below).

With *beer* essentially the same considerations apply as for wort, but though the dilution error is less, matters are somewhat complicated by the presence of alcohol and carbon dioxide. The former has relatively little effect in the concentrations in which it occurs in beer. The presence of carbon dioxide, however, must be taken into account, since removal of it by a stream of hydrogen may upset the carbonate-bicarbonate equilibria, which play a part in controlling the buffer-effect, without greatly increasing the pH. This source of error may be eliminated by use of the correct mixture of hydrogen and carbon dioxide, though this is troublesome, and for highly carbonated liquids even impossible. An alternative, which gives at any rate comparable results is to toss the beer to and fro between two beakers until the excess of gas is removed.

Fortunately, however, the quinhydrone electrode, the use of which was suggested by the writer,[63] gives excellent results in beer, which, of course, is always more acid than pH 8. Stockhausen and Rothenbach,[64] and also Mündler,[65] found quite small differences in comparative experiments with different types of these electrodes.

In exceptional cases, and for highly accurate work, even the quinhydrone electrode may be suspect. Bijlmann and Katagiri [66] pointed out that in the presence of glucose, which has a specific poisoning effect on the quinhydrone electrode, the hydro-quinhydrone (p. 48) electrode may be used. This electrode also gave good results in phosphate-bicarbonate solutions saturated with carbon dioxide at 1 atmosphere pressure.

For rough colorimetric measurements [73, 88] advantage may again be taken of the good buffering power of beer, and the sample diluted eight times (pale beers), sixteen times (dark beers) or forty times (porters). In addition, the beer may be titrated in stages with neutral red (pH 7·1) and then with phenolphthalein (pH 9·2).

Kolbach [67] has shown (cf. Hopkins and Kelly, *loc. cit.*) that the complete buffer effect of beer (or wort) is summed up by determinations of (*a*) pH value ; (*b*) titratable acidity to pH 7·1 (electrometrically or with neutral red indicator) ; (*c*) titratable alkalinity to pH 4·3. Buffers between pH 5·7 and 7·1 are chiefly phosphates, whilst between pH 4·3 and 5·7 they are degradation products of proteins, organic acids, and their salts. Formol titration (p. 116) gives the protein degradation products separately. Heintz [67] considers pH 4·0 a more suitable value for

titratable alkalinity, and, in addition, determines the buffer-value after removal of phosphates by means of solutions of barium chloride and hydroxide. The acidity-titration to a particular pH value may best be found by Kolbach's method (p. 123), which was devised originally for wort and beer.

It should be noted that fined beers should normally be used for these determinations, especially if the determination is intended to indicate the degree of stability. Moreover, they are free from the objections attached to turbidity and suspended or colloidal particles. Parsons considers pH 4·2 the least acid reaction which should be shown by a beer, as more alkaline beers are liable to development of sarcina (pH 5–6). There is no relation between the acid flavour of beer and its pH value (p. 126).[68]

Carbon dioxide in beer or other liquids may be determined colorimetrically by De Clerck's method,[69] in which 15 c.c. of 0·1*N* sodium hydroxide solution, 10 c.c. of cold beer, and 2·5 c.c. of water are placed in a tube of a Walpole colorimeter behind a similar mixture in which the water is replaced by 2·5 c.c. of phenolphthalein solution. To each of two similarly-placed adjacent tubes are added 25 c.c. of borate buffer (pH 8·4) and 2·5 c.c. of either water or phenolphthalein, and 0·1*N* hydrochloric acid is then added to the tube containing the beer and indicator (1) before, and (2) after removal of carbon dioxide by bringing the solution just to the boil. The difference in amount is equivalent to the volume of 0·1*N* sodium hydroxide solution required to convert the carbon dioxide into bicarbonate at pH 8·4, and 1 c.c. of 0·1*N* NaOH≡0·0044 grm. CO_2.

Sugar.—Ph control is used in every stage of the manufacture of sugar, but the nature of the liquids employed raises problems peculiar to this case. Sucrose is inverted with progressive ease as the acidity increases from pH 6·5 to 3, while the reducing sugars are transformed into glucinic acids at the boiling-point between pH 8 and 11, and the transformation is most rapid in alkaline solutions. Raw cane juice has normally a pH of about 5·5 defecation and sulphitation occur at pH 7–8·5, calcium sulphite and phosphate precipitate at pH 5·5 (Britton[71]). The pH limits for the first and second carbonations are 11·3 and 8·1 respectively, and these are also the precipitation points of pectins and gums and of calcium carbonate respectively.

Ph control or electrometric titration for defecation purposes may be carried out conveniently with the quinhydrone electrode so long as pH 8 is not exceeded, and comparison may be made with the curves obtained by Britton, which show the precipitation of calcium phosphate by lime water in the presence of phosphoric acid or sucrose. Walton, McCalip, and Hornberger[72] found that with this electrode the pH of a syrup whose gravity

was more than 40° Brix was always lower than that of the same sample diluted to 15° Brix. This is mentioned because syrups diluted to 10° or 15° Brix are usually taken for pH determinations. A tungsten electrode (Parker, see below) has been found suitable for strongly alkaline solutions, but requires calibration in terms of pH value. The quinhydrone electrode may be used with raw sugars, which are distinctly acid, and also, of course, for the determination of the pH of inversion. An antimony electrode also has been suggested, and the pH is then given in terms of the *E.M.F.* at 14° by the expression $0{\cdot}052+0{\cdot}057\,.\,E$.

For sulphitation liquors the presence of sulphur dioxide means that electrometric methods must be abandoned in favour of indicators, and one of the spotting or capillator methods [73] described on p. 93 will probably be found most convenient. Where sulphitation is carried out at pH 3·5–4·0, brom phenol blue may be used. Brom thymol blue does not always give reliable results with sugar solutions.

For carbonation control reference may be made to other liquids in which free carbon dioxide is present (see *Beer*, p. 123, *Water*, p. 135).

Automatic apparatus (p. 57) is being extensively adopted, particularly in America, for pH control in the sugar industry. Thus, Parker [74] has described a tungsten electrode made from a glass tube coated with manganese oxide (Mn_2O_3) around which was wound a tungsten wire passing inside the tube to a mercury contact. Both this and the calomel electrode, the outlet of which was suitably protected, were inserted in the same closed chamber through which the sugar juice flowed, and a continuous record of the pH values was thus obtained, the *E.M.F.* of the cell being calibrated directly in pH values. An electromagnetic valve was inserted to control the addition of reagent, and the method was found very suitable for alkaline solutions produced by lime defecation. The principal difficulty in such cases is the lack of an indicating electrode which gives continuous yet reliable readings. Even bare tungsten wire, which is the best type of electrode available for the purpose, is easily poisoned, especially by particles of solid matter in the flowing solution, and has to be replaced every day. Holven [74] obtained the best results with raw sugar liquors, but had less success with solutions produced at other stages of the manufacture.

Molasses are tested by any of the usual colorimetric methods suitable for undiluted coloured solutions (see p. 99). The optimum pH value for fermentation into alcohol is 5·0, and decolorising charcoal has its maximum effect at pH 7.

Vinegar has a pH of 3–4 (0·1*N* acetic acid has pH 3·0).

Wines [70] present no special difficulties.

Foodstuffs

For *Bakery, Brewing, Sugar* and *Vinegar*, see under *Fermentation Industries*.

Boric Acid.—The determination of boric acid,[75] which has become of great importance in view of the recent tendencies to prohibit its use as a preservative for foodstuffs, depends on the fact that the acid HBO_2,H_2O($K=6\times10^{-10}$) is monobasic and extremely weak, and gives an indefinite end-point with phenolphthalein at about pH 11. But if glycerol or mannitol is added, a complex compound with boric acid is formed in solution, and the end-point brought to about pH 5–6, so that phenolphthalein may be used with safety. The details of the method as used in the Government Laboratory[76] are as follows :—

A mixture of sample neutralised to phenolphthalein with 2 c.c. of *N* sodium hydroxide solution is dried, the fat extracted twice with ether, the extracts shaken with 5 c.c. of the *N* alkali and then with 5 c.c. of water, and the washings added to the dry residue. More *N* alkali is then added till not less than 2 c.c. per grm. of dry solid are present, the mixture dried, charred, and extracted with 10, 5, 5 and 5 c.c. portions of water and the liquid filtered into a 100 c.c. flask. The residue is ashed, dissolved in hydrochloric acid, and added to the liquid in the flask with enough additional acid to dissolve any precipitate. Carbon dioxide is removed on the water-bath and 5 c.c. of *N* calcium chloride solution and 5 drops of phenolphthalein added to the cool liquid, followed by sufficient *N* alkali to produce a slight permanent precipitate (calcium phosphate), and 0·1*N* alkali to produce a faint permanent pink colour on shaking. The mixture is made up to 100 c.c., shaken, filtered, and sufficient 0·1*N* sulphuric acid added to 75 c.c. to render it acid to 1 drop of methyl orange. Carbon dioxide is boiled off, 10 drops of phenolphthalein added, and the liquid exactly neutralised to methyl orange. It is then titrated to phenolphthalein neutrality with 0·1*N* sodium hydroxide solution in the presence of 0·5 grm. of mannitol or 33 per cent. by volume of glycerol. (In the former case more mannitol should be added at the end-point until the red colour is no longer destroyed.) The blank on the reagents is deducted from the titration, and 1 c.c. 0·1*N* alkali$\equiv$0·0062 grm. H_3BO_3. The residual precipitate should be dissolved in acid and reprecipitated, and boric acid shown to be absent from the filtrate.

Fruit Juices[52, 77].—The quinhydrone electrode is usually employed, since fruit juices are relatively acid in reaction. It rapidly attains its equilibrium, though McKibbin and Pugsley[12] have recorded cases when the results obtained are slightly high in comparison with those obtained by the hydrogen electrode or colorimetric method. The correspondence between acid taste and pH assumed by early workers is so modified by the presence in fruit juices of other compounds which contribute to the flavour

that it is not perceptible.[78] The pH values of some fruit juices are shown in Fig. 2, p. 12.

Milk Products.—The quinhydrone electrode gives satisfactory results with *cheese*, *cream*, *milk* and *whey*, especially when a gold or gold-plated wire (p. 7) is substituted for platinum.[12, 79]

According to Watson,[80] and also Knudsen and Dawson,[80] in the case of *cheese* and *whey* holes should be made in each side of the sample, the whey pipetted out and well cooled. The electrode is then moistened with it, dipped in powdered quinhydrone, and inserted in an open glass tube (A, Fig. 39), and the whey drawn up around it. The tube and electrode are then placed in the potassium chloride vessel (B). If the solid cheese is used, 0·1 grm. of quinhydrone is rapidly mixed in a mortar with 5 grms. of cheese, and packed round the electrode in the glass tube.

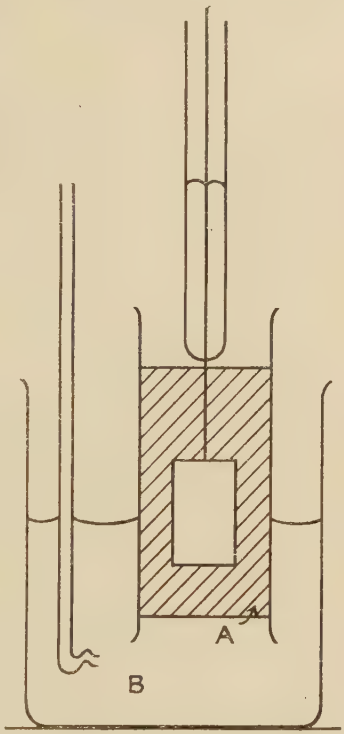

FIG. 39.

In the case of *milk*, colorimetric methods are used when the electrometric (quinhydrone) method is not convenient, and, in fact, they are usually found quickest and sufficiently accurate. Brom thymol blue is a useful indicator for the detection of the development of small amounts of acidity or alkalinity, and the change in pH of the sample and indicator mixture contained in sterile test-tubes is observed during 24 hrs. According to Van Slyke,[81] normal milk gives a green-blue colour with brom cresol purple (pH 6·1), the colour being brighter if the milk has been heated above the temperature of pasteurisation. Alkaline salts and certain udder diseases (mastitis) are denoted by a dark blue colour. Phenol red in the presence of a little potassium oxalate to enhance the colour (Kolthoff), is also used, but alizarine is not recommended.

Where the colorimetric method is used for thick liquids (*milk*, *whey*, *cream*) which require to be diluted (*e.g.*, 20-fold), Sharp and

McInerey,[81] showed that if dialysis is used, this process compensates any indicator error, the dialysate appearing to have a pH equal to that of the sample, instead of being about 0·05 higher. A correction may easily be applied by plotting the pH and the logarithm of the volume for several dilutions and then finding the difference in pH between that of the original milk and of the diluted liquid used (cf. Atkins and Thompson, p. 99). The relation between pH and titratable acidity produced on souring is approximately exponential.[82] Whittier [83] has shown that the titration curves of milk indicate a maximum buffering power at pH 5·5. Since caseinogen exerts its

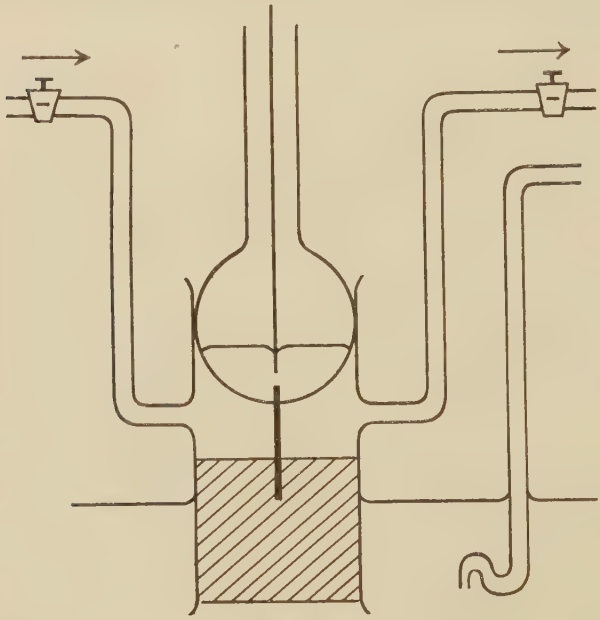

Fig. 40.

buffer action at pH 5·2, it would appear to be an important buffer-constituent of milk, especially as the addition of rennet, which converts it into casein, alters the whole shape of the curve.

Tinned Foods, Pastes, etc.—Where the sample is solid or semi-solid indicators are useless, and the electrometric method described by Monier-Williams [84] is usually employed. As Fig. 40 shows, the sample in paste form is tightly packed into an open glass tube as in the method for cheese (Fig. 39), but so that the paste just reaches the bottom end of the platinum wire electrode. Hydrogen is then passed over the surface and the tube dipped in a beaker of saturated potassium chloride solution, and the

measurements taken against a saturated calomel electrode placed in the same solution.

The results obtained, which are of importance for the study of the growth of *B. botulinus*, included the pH values of the following mixed tinned foods: Rice, tomato, and onion (5·4), bean, cabbage, potato, turnip, and onion (5·36), steak, kidney, and onion (5·86), rhubarb (2·73), chicken, ham, and tongue (5·4), ham and chicken or tongue (5·6), salmon and shrimp (5·8), salmon, shrimp, and anchovy (5·5), shrimp (6·4).

Leather Industry

One of the earliest important communications on pH determination was a paper by Sand and Law,[85] which described an electrometric apparatus suitable for the leather industry. The hydrogen electrode was recommended, and the apparatus and procedure were substantially the same as described in Part II, Chapters II and III.

More recently, colorimetric methods with Clark and Lubs' indicators have come into vogue for rapid routine work. Thus Atkins and Thompson[86] use the method described on p. 99 to determine the effect of dilution on the pH of coloured tan liquors, while for more accurate work Bruère[87] has suggested an electrical comparator (see p. 95), in which light from an iron arc passes in succession through a condenser, a colour filter, and the solution, and falls on a photoelectric cell in series with a battery and a galvanometer. The galvanometer deflections are expressed as percentages of the deflection obtained when distilled water is used.

In another routine method,[88] the indicator-solution is mixed with an equal volume of coloured test-solution in a depression on a white tile, and the colour matched against a colour chart prepared from solutions of known pH. Similarly, in Wulff's method[89] transparent absorbent material, which adsorbs $H^{\cdot}$ and OH' ions more rapidly than an indicator, is dipped in the mixture of solution and indicator, under standard conditions of time, etc., dried, and compared with a set of standards. Such methods, although unaffected by any colour or turbidity of the liquid, are dependent on the accuracy of the standards and should only be used when these have been carefully checked. The accuracy of 0·05 pH claimed by one worker[89] appears much higher than would ordinarily be expected.

Pleass[87] finds the compensated capillator the most simple and rapid method when an accuracy of 0·2 pH is desired, except for lime liquors. The hydrogen electrode is suitable for liquors of strength less than 60° Bk. and in the absence of poisons, but the glass electrode is preferred to all others. Typical titration curves are discussed.

Leather Extracts [90] are best made either by soaking 1–10 grms. of leather in 100 c.c. of cold 0·1*N* potassium chloride solution for 24 hrs., or by heating it under a reflux condenser after digesting it with 10 times its weight of water for 15 hrs., and filtering the cooled liquid. By the use of various amounts of leather and the same amount of extracting liquid, data may be obtained for the calculation by extrapolation of the pH of the leather containing its natural amount of moisture.

One-Chrome Liquors may be examined electrometrically by the hydrogen or quinhydrone electrodes, which have been proposed by Innes [91] as the official methods.

Britton [92] points out that it is interesting to note that the basic extent of basic chromium sulphate $Cr(OH)_x(SO_4)_y$ liquors increases with the pH from pH 1·16 to 3·38, most efficient tanning being produced at pH 3·0. Such liquors, however, are badly buffered. The *basic extent* (not "basicity") is the percentage weight of chromium in combination with OH-groups compared with that combined with both OH- and SO_4-groups.

McCandlish [93] introduced the *precipitation figure* (*p*) as an indication of the tanning power of chrome liquor. The liquor is cleared with kaolin and filtered, and 10 c.c. titrated with 0·1*N* sodium hydroxide solution till precipitation ensues. This is the danger-point for basic liquors, but in practice tanning usually proceeds most rapidly for solutions having the lowest precipitation figure. Burton, Wood, and Glover [94] studied the corresponding changes in pH, using violet and green (*i.e.*, boiled) chrome alum solutions, and Britton calculated from their data that 5, 10, 50, and 100 grms. of alum per litre corresponded respectively with pH 3·08, 3·08, 2·91, and 2·73, and *p* 0·33, 0·29, 0·26, and 0·26 for the former, and with pH 2·12, 2·03, 1·69, and 1·52 and *p* 0·50, 0·47, 0·41, and 0·39 for the latter. Schindler and Klanfer [95] take the *precipitation quotient* as the change in pH required to diminish *p* by 1 c.c. of 0·1*N* sodium hydroxide solution in a liquor containing 1 grm. Cr_2O_3 per litre; *i.e.*, it equals (pH at precipitation point − pH of liquor) × *p*.

Gelatin and Glue have also been the subject of a recent report [91] on the determination of pH value. By virtue of their NH- and NH_2-groups, and of their COOH-groups respectively, both gelatin and collagen act as bases at pH values below the isoelectric point (pH 4·6) and as acids above it. Their pH values are determined by electrometric titration, or colorimetrically, with nitrophenol indicators.

Metallurgy [37]

Analysis. — Electrometric titration (p. 10) is particularly suited to metallurgical analyses.

Corrosion.—According to the recent theories of Evans [96] and others, corrosion is essentially an electrochemical phenomenon, and it is to be expected that pH determinations will shortly begin to play a part in its control. Up to the present, however, no special methods have been adopted, and any of the ordinary procedures suitable to the solution concerned may be used. Attempts to relate change in pH value of the corroding medium with the degree of corrosion have not been entirely successful.[97] Probably other factors have to be taken into account.

Electro-Deposition.—It will be appreciated from Chapter I of Part II that the electrode-potential of a particular metal and the pH of the solution in which it is immersed are important factors on which the tendency of the metal to deposit depends. Other factors, however, are the cathodic polarisation, the hydrogen over-voltage, the current-density of the current used, and the pH of precipitation of the hydroxide of the metal. Table 3 on p. 143 shows the electrode-potentials of some common metals, and the corresponding precipitation-potentials (as pH values) of their hydroxides given by Britton.[98] It will be seen that for base metals less noble than hydrogen (*e.g.*, iron, cobalt, nickel, cadmium) these two values are relatively very close, and that deposition will be rendered unsatisfactory by liberation of hydrogen and by precipitation of the hydroxides. Hence the necessity for the use of buffers to keep the pH constant during deposition, and also, consequently, for pH control. Thus, particularly in *nickel-* and *cobalt-plating*, ammonium chloride, sulphate or fluoride with boric, tartaric, or citric acid have been used [99] at pH 5·6–6·0 with great success, for nickel hydroxide is precipitated at pH 6·7 and cobalt hydroxide at 6·8. In both cases the quality of the deposit is affected below pH 4·5–5·0. Hughes [99, 100] has summarised the baths suitable for *iron*, and Allmand and Campbell [99, 101] have worked on *manganese* deposition. When the solution is well stirred, the pH value may be nearer the higher limit. Sulphuric acid is preferable to boric acid when the change in pH during electrolysis is opposed by additions of small quantities of acid as required.

It should be pointed out that exact agreement between the pH values obtained by the electrometric and colormetric methods is seldom essential in such cases, nor does it matter if the value found is not the true pH value. The reason is that the plater requires pH control only as a means of regulating his bath, and so long as he knows what the variations in pH imply he is able to make the necessary rapid adjustments. The colorimetric method, therefore, corrected for salt error and temperature, is again suggested as the routine method, with the other for periodical control.

Hothersall [99] has found thymol blue, brom phenol blue, methyl red, brom cresol purple, and brom thymol blue suitable for the range pH 1·2–7·6 if compensation is made for the natural colour of the solution by the usual methods (p. 99). Any variation of the colorimetric method may be used.

Brewer and Montillon,[102] in a review of the electrometric methods, concluded that for general purposes the quinhydrone electrode is preferable. The oxygen electrode cannot be used in chromium and acid iron baths on account of oxidation, while the antimony-antimonious oxide or lead dioxide electrodes (particulars of which are given) are suitable in non-acid oxidising baths and in the absence of chromium.

Warm baths should, of course, always be cooled to 20° for comparative determinations. Thus, a double-salt solution for nickel-plating has a pH 0·4 unit lower at 35° than at 20°.

Paper

Litmus has long been used for control purposes in paper manufacture, but is rapidly being displaced by indicators which respond to a more appropriate pH range, and so provide a higher degree of precision. Clark and Lubs' series are usually found satisfactory. With *sulphite liquors*, in fact, which are very acidic, the electrometric method cannot be used, and Escourrou and Carpentier [103] were able to follow the pH changes during working by applying the colorimetric method to the used liquors. Soft, readily-bleachable pulps were obtained below pH 2. Graap [104] has suggested electrometric methods for the control of the lime and sugar contents of sulphite liquors.

The *bleaching process* gives the whitest pulp with an alkaline bleach. Bergquist [105] employed the pH value of bleaching solutions as a control of the buffering power of the hypochlorous acid. Wulff's colorimetric method [89] (p. 90) was used, but only 20–30 secs. immersion is required on account of the bleaching effect of the test-solution. If the colour is weak several transparent strips of indicator material may be immersed, dried, and superimposed for matching purposes. An accuracy of 0·1 pH is claimed between pH 2·6 and 9·0.

The purity of the alkaline *size* prepared by boiling resin with alkali (with the consequent conversion of abietic acid, $C_{19}H_{29}COOH$, into sodium resinate, $C_{19}H_{29}COONa$) may be tested by titration of a solution in warm alcohol by an alcoholic solution of an acid with phenolphthalein (pH 8·5) or thymol blue (pH 9·0) as indicator.[106] Such size contains a 15–25 per cent. excess of alkali. The optimum pH for sizing has been

given by Roschier [107] as 3·9–5·5 for ordinary paper and 5·8 for Kraft, which requires less resin, though Britton,[107] in a discussion on the influence of pH on sizing, points out that the aluminium sulphate is precipitated as hydroxide at pH 4·0–4·1.

The *filling* and *dyeing* (p. 119) of paper are also dependent on the pH value. Roschier (*loc. cit.*) gives pH 5·0–5·5 as the optimum reaction for the preparation of clay fillings. Optimum dye absorption by clays occurs at pH 4·0. It should be noted that even paper in a pure form such as filter paper will yield sufficient saline matter to alter the pH of distilled water when extracted. Atkins [7] found that well-washed, acid-extracted papers have pH 4·8, whilst unextracted papers have pH 7–7·6. This may introduce an error, *e.g.*, in soil work (p. 104), or when a badly-buffered solution is being filtered.

To determine the pH value of the *paper* itself 1 grm. of sample is cut up, shaken with 50 c.c. of boiled, distilled water in a 100 c.c. flask, and the volume made up to the mark after digestion for 1 hr. on the water-bath. The filtered extract may then be tested by the colorimetric method (Wulff's modification,[89] see p. 90) or by the electrometric (quinhydrone) method. Alternatively, the paper itself may be minced and mixed with the quinhydrone and water and measured directly, or else impregnated with indicator solution and the colour compared with standards prepared under the same conditions from pure paper and buffer solutions. Pure paper should have a pH value of about 6·0–6·1.[108]

The *acidity* of finished paper is sometimes important when the paper is to be used (*e.g.*) for packing metal articles in a damp climate. Rough corrosion tests on paper in contact with metal give an indication of the state of the paper, but the acidity may also be determined by titration of 100 grms. of paper with 0·1*N* sodium hydroxide solution after steeping in cold water for 24 hrs. A better form of control, which eliminates any acidity from the filling, is a pH determination on the aqueous extract by the colorimetric method. Kalb and Falkenhausen [109] consider a paper with pH less than 5 injurious to metal.

Celluloid.—Ellington [110] determines the pH value (surface acidity) by shaking 2 grms., ground to pass a 0·032 in. sieve, with 10 c.c. of water and 0·5 c.c. of a 0·2 per cent. solution of dimethyl aminoazobenzene in a test-tube (0·5 in. diameter) closed with a cork wrapped in tinfoil. After some hours the colour is matched against standards, prepared in a similar way, from 0·1 grm. of pure, white, soft filter-paper, and buffer solutions of pH 1·8–5·0.

Pharmacy

The applications of pH determinations to pharmacy are discussed by Caldwell and others.[111] The methods involved are usually those already described (see *Analysis*).

Alkaloids.—Kolthoff [112] obtained good results in the titration of alkaloids with a quinhydrone electrode, though certain alkaloids have been said to act as poisons towards the hydrogen electrode. The mercury electrode has also been used.

Ordinary titration may, however, be used if the end-point of the indicator is chosen carefully so as to correspond with the ionisation constant of the alkaloid. The importance of the correct choice was demonstrated by McGill [113] and the ionisation constants of some common alkaloids are given in Table 1, p. 141. For example, Rasmussen and Schou [114] recommend methyl red (pH 6) for atropine, brucine, cinchonine, codeine, morphine, nicotine, and strychnine; methyl orange buffered to pH 4·2 for narcotine; *p*-nitrophenol (at pH 6·2) for quinine; brom cresol purple and hæmotoxylin for quinine; and brom phenol blue for atropine and morphine. Where ionisation occurs in two stages the end-point of the titration may be taken at the first, since the second stage usually represents a comparatively weak degree of dissociation. Alkaloid salts may be titrated directly with alkali to the litmus end-point.

Britton [115] points out that pH control may also be employed in the *separation of alkaloids*, having different ionisation-constants. If, instead of free alkali, a buffer solution of the correct pH is added to a mixture of two alkaloids it is possible to reach the end-point of that alkaloid having the smaller ionisation-constant. It may then be extracted with an organic solvent, and the other alkaloid treated separately.

Water

Water is normally a colourless liquid, and is therefore most conveniently tested by colorimetric methods. With sea-waters, however, there is a large salt error. Various aspects of the pH value of water have been discussed by the writer.[116]

Boiler Water.—Control of boiler waters is usually of importance in connection with softening processes, and to ensure that the source of supply is remaining constant. The total salt content is therefore of greater interest than the actual pH, though it is very unlikely that a change in the former will not produce a change in the latter. Rapid (colorimetric) pH determinations may therefore be made in the usual way, though one of the automatic forms of apparatus is obviously appropriate

in such cases. As a matter of fact, it is usual to employ conductometric methods in which the electrical conductivity of the water is measured continually, any change in salt content being accompanied by a corresponding change in conductivity which is recorded on a suitable instrument and made to actuate an alarm or correcting relay [117] (see p. 112). See also **Natural Waters.**

Distilled Water.—The theoretical relationship of distilled water to "pure" water was discussed on p. 125. The pH of distilled water is of interest when large quantities are being prepared continuously, as a check on the absence of contamination, and may with advantage be carried out periodically in every laboratory. It has already been explained that on account of the bad buffering powers of distilled water, its exact pH is not of the first importance when it is used for the preparation of solutions, or otherwise for pH work.

The actual pH will depend on the still used, the age of the water, and the vessel and atmosphere in which it is stored.[118] A good, freshly-distilled water will have pH 5·5–6·0, but this may fall as low as pH 5·0 on account of absorption of carbon dioxide. Distilled water boiled to expel this gas, and stored in paraffin-coated vessels in an atmosphere neutralised by bubbling the air through lime water, may have pH 6·0–6·5.

It has already been pointed out (p. 87) that the pH of a badly-buffered liquid will be influenced by the acidity of the indicator itself. Thus methyl red, which is itself an acid ($K=9\times10^{-5}$), will give results on the acid side. The neutral salt ("Methyl Red, Water Soluble") is therefore used.

Methyl red is purified by slowly adding a filtered solution of 300 grms. in 145 c.c. of 33 per cent. sodium hydroxide solution and 1 litre of water at 60°, to boiling 33 per cent. hydrochloric acid. The blue crystals of methyl red hydrochloride which separate from the cool solution are filtered off, washed in 1 litre of 10 per cent. acid, and dissolved in 160 c.c. of 33 per cent. sodium hydroxide solution and 1000 c.c. of water, and the solution filtered and cooled to 20°. Shining yellow spangles are then precipitated by addition of 50 grms. of sodium chloride, and are filtered, washed with a little water, and dried below 40° to orange-red crystals. According to Fairbrother,[119] this is the best method of preparation.

The neutralised form of brom thymol blue (Table 5, p. 145) may also be used, and a good neutral water, which is alkaline to methyl red, should give a green colour with this indicator.

Drinking and Mineral Waters.—Such waters are usually alkaline (pH 7–8·5) and contain dissolved carbon dioxide in equilibrium with bicarbonates and carbonates. Johnston's data [120] show that the pH of water in equilibrium with solid

calcium carbonate varies from 8·4 to 8·1 for partial pressures of carbon dioxide ranging from 0·0002 to 0·0005 atmospheres.

Methyl red, brom cresol purple, neutral red (or phenol red) and thymol blue (or cresol phthalein) are therefore the indicators best suited to the pH range if the colorimetric method is used. Carbon dioxide in solution may be determined colorimetrically by the method described for beer (p. 124). Where the system carbonate-bicarbonate is present, the reaction is alkaline even to phenolphthalein. Indicators are, of course, out of the question for use with *chlorinated water*, but readings obtained with the hydrogen electrode are reliable if they are taken rapidly.

The presence of the carbon dioxide renders the hydrogen electrode suspect in such cases, though the devices for eliminating its effects described on p. 70 may be used. Automatic pH control should, however, prove useful in conjunction with processes for the treatment of water or of turbid liquids (*e.g.*, sewage), especially in the latter case, where an optimum pH for precipitation exists. The pH of supply water may vary slightly from day to day.

Sea-water.—The pH of sea-water varies within remarkably small limits all over the world (except, of course, in the Dead Sea), and is pH 8·0–8·4 at the surface. There are additional slight variations (*e.g.* with depth, and at the estuaries of rivers), and their effect on marine life and on the precipitation of suspended matter (which may silt up a harbour) is important. This constant pH value is due to the carbon dioxide-carbonic acid-bicarbonate equilibrium produced by solution of atmospheric carbon dioxide in the water at pH 8·2 or more to an extent proportional to the constant partial-pressure of the gas in the air. The gas dissolves to form the weak acid H_2CO_3, thus $H_2O+CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons H^{\cdot}+HCO_3'$, which, with its highly dissociated sodium salt, forms a buffer mixture and keeps the pH constant.

Here, again, therefore, the colorimetric method is usually preferable, but notice must be taken of the high salt content of the water, and allowance made for the salt error. This has been determined for salt solutions of various strengths (Table 6, p. 146). Michaels has found *meta*-nitrophenol suitable for the purpose if only small quantities of it are taken, but among the Clark and Lubs range, cresol red is recommended by Seiwell,[121] who gives the correction −0·27 pH for salinities of 32–35 per 1000. According also to Ramage and Miller [122] the correction for the salt error of cresol red in water containing 5 to 35 parts per 1000 of sea-salts is −0·11 to −0·27 pH. For sea-water (0·55*N* sodium chloride) the value −0·18 may be taken.

The mean pH values of the English Channel and North Sea

were found by the *Carnegie* (1928) expedition to be 8·03 and 8·11 respectively. The open sea has a pH value of 8·1 in winter, while phyto-plankton raise it to 8·3 in summer by removal of carbon dioxide. In the North Atlantic the pH varies from 8·35 at the surface to 7·87 at a depth of 3000 metres.

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PART V

TABULATED DATA

In the following pages an attempt has been made to collect together in tabular form for the sake of convenience, all the data and information normally required in the measurement of hydrogen ion concentration by the electrometric or colorimetric methods. Tables of logarithms and a nomogram for the interconversion of millivolt-readings and pH values are included.

References to the sources of the data, which are many, will be found at the end of the Parts concerned, but special acknowledgment must be made to Clark's *Determination of Hydrogen Ions*. Only the latest and most reliable information has been included.

TABLE I.

Ionisation Constants of Acids, Ampholytes and Bases at 18° *C.*

Acids.	p*K*	Bases.	p*K*
Acetic	4·74	Acetamide	14·5
Arsenic	2·30	Aconitine	5·9
Arsenous	9·22	Ammonia	4·75
Benzoic	4·18	Aniline	9·46
Boric	9·21	Atropine	4·40
Carbonic	6·42, 10·22	Brucine	6·04, 11·70
p-Chlorphènol	9·20	*m*-Chloraniline	10·5
Chromic	6·40	*p*-Chloraniline	9·8
Citric	3·0, 4·5, 5·65	Cinchonidine	5·80, 10·03
Dextrose	12·30	Cinchonine	5·9, 9·9
Dichloracetic	1·33	Cocaine	5·60
Formic	3·69	Codeine	6·05
Fumaric	3·00, 4·58	Conine	3·10
Gallic	4·00	Diethylamine	2·95
Glutaric	4·30, 4·55	Dimethylamine	3·26
Glycerol	14·20	Ethylamine	3·28
Gycol	14·20	Hydrazine	5·65
Glycollic	3·82	Isoquinoline	8·96
Hydrazoic	4·8	Methylamine	3·35
Hydrochloric	($K=10^7$)	Narcotine	7·82
Hydrocyanic	9·12	Nicotine	6·2, 10·9
Hydrogen peroxide	11·62	*o*-Nitraniline	14·0
Hydrogen sulphide	7·22, 14·70	*m*-Nitraniline	11·4
Hypochlorous	7·40	*p*-Nitraniline	12·0

TABLE 1—*continued.*

Acids.	*p*K	Bases.	*p*K
Hydroquinone	10·00	Novocaine	5·2, 11·8
Lactic	3·84	Phenyl hydrazine	3·80 (40°)
Maleic	6·5	Pilocarpine	7·2, 12·6
Malic	5·11	Piperazine	4·1, 8·3
Malonic	2·70, 5·36	Piperidine	2·80
Mannitol	13·5	Pyridine	8·85
Monochloracetic	2·8	Quinine	5·96, 9·70
m-Nitrophenol	8·4	Quinoline	9·5
o-Nitrophenol	7·3	Strychnine	6·0, 11·7
p-Nitrophenol	7·3	Triethylamine	3·25
Nitrous	3·41	Trimethylamine	4·20
Oxalic	1·42, 3·80	Urea	13·85
Phenol	10·00		
Phenyl acetic	4·27	Ampholytes.	
Phosphoric	2·0, 7·0, 11·6	Alanine	9·7, 11·3
o-Phthalic	2·9, 5·4	Apomorphine	7·01, 8·92
m-Phthalic	3·5, 4·6	Aspartic acid	3·8, 9·9
Picric	0·8	Ecgonine	11·1, 11·2
Propionic	4·80	Glutamic acid	4·4, 9·8
Salicylic	2·98	Glycine	9·7, 11·6
Succinic	4·17, 5·40	Leucine	9·7, 11·6
Sucrose	13·0	Morphine	6·13, 9·85
Sulphuric	1·77	Narceine	9·3, 10·7
Sulphurous	1·79, 5·3	Phenyl alanine	8·6, 11·9
d-Tartaric	3·0, 4·2	Tyrosine	9·4, 10·4
Uric	5·80	Valine	9·7, 11·7

NOTE.—Where two or more values of p*K* are given, they refer to the first and second (or third) ionisation constants of poly-acids or bases. Where only one is given in the case of poly-acids or bases it refers to the last dissociation of the substance. The choice of indicator is, of course, based on this last value (see p. 108).

TABLE 2.

Buffer Solutions (20° C.)

pH	*a*	pH	*b*	pH	*c*
1·0	97·0	2·2	46·60	4·0	0·40
1·2	64·5	2·4	39·60	4·2	3·65
1·4	41·5	2·6	33·00	4·4	7·40
1·6	26·3	2·8	26·50	4·6	12·05
1·8	16·6	3·0	20·40	4·8	17·60
2·0	10·6	3·2	14·80	5·0	23·75
2·2	6·7	3·4	9·95	5·2	29·85
		3·6	6·00	5·4	35·35
		3·8	2·65	5·6	39·75
				5·8	43·10*
				6·0	45·40*
				6·2	47·00*

TABLE 2—*continued.*

pH	*d*	pH	*e*	pH	*f*
5·8	3·70	7·8	2·65*	10·17	40
6·0	5·65	8·0	4·00	10·35	30
6·2	8·55	8·2	5·90	10·55	20
6·4	12·60	8·4	8·55	10·86	10
6·6	17·75	8·6	12·00	11·04	6
6·8	23·60	8·8	16·30	11·36	0
7·0	29·60	9·0	21·30		
7·2	34·95	9·2	26·70	pH	*g*
7·4	39·40	9·4	32·00		
7·6	42·75	9·6	36·85	11·29	25
7·8	45·20*	9·8	40·80	11·77	50
8·0	46·85*	10·0	43·90	12·06	75

KEY.

Clark and Lubs. *a*—c.c. 0·2*N* HCl+50 c.c. 0·2*M* potassium chloride.
b— ,, ,, ,, pot. hydrogen phthalate.
c— ,, NaOH ,, ,, ,,
d— ,, ,, ,, pot. dihydrogen phosphate.
e— ,, ,, ,, boric acid.

Kolthoff. *f*— c.c. 0·1*N* HCl+100 c.c. 0·1*M* sodium carbonate.

Ringer. *g*—c.c. 0·1*N* NaOH+50 c.c. 0·15*M* disodium phosphate.

The above mixtures are all diluted to 200 c.c.

* Asterisked mixtures are those whose accuracies have been questioned (see p. 22).

TABLE 3.

Electrode Potentials of Elements and Radicals, and pH Values for the Precipitation of Metal Hydroxides.

Metal or Radical.	*E* volts.	pH
Potassium	+2·6	—
Barium	+2·6	—
Strontium	+2·5	—
Sodium	+2·4	—
Calcium	+2·4	—
Magnesium	+1·3	10·49
Aluminium	+1·03	4·14
Manganese	+0·82	8·4–8·8 ($Mn^{..}$)
Zinc	+0·51	5·20
Chromium	+0·26	5·30
Iron ($Fe^{...}$)	+0·20	2 (?), ($Fe^{..}$, 5·49)
Cadmium	+0·16	6·7
Cobalt	+0·05	6·81
Nickel	−0·02 ?	6·66

TABLE 3—*continued.*

Metal or Radical.	*E* volts.	pH
Lead	−0·12	6·0
Tin ($Sn^{\cdot\cdot}$)	−0·14	2 (?)
Hydrogen	−0·24	—
Arsenic	−0·53	—
Copper ($Cu^{\cdot\cdot}$)	−0·58	5·4
Bismuth	−0·63 ?	—
Antimony	−0·71	—
Iodine	−0·78	—
Mercury	−0·99	7·3 ($Hg^{\cdot\cdot}$)
Silver	−1·04	9·0
Platinum	−1·10 ?	—
Bromine	−1·32	—
Oxygen	−1·36	—
Chlorine	−1·50	—
Gold	−1·7	—
OH	−1·96	—
SO_4	−2·2	—
HSO_4	−2·9	—
Zirconium	—	1·86
Beryllium	—	5·69
Cerous	—	7·41

(See pp. 33 and 115.)

TABLE 4.

Potentials in Millivolts of Calomel and Quinhydrone Electrodes at Various Temperatures in Relation to the Normal Hydrogen Electrode.

Temp. °C.	0·0001983 × (t° C. + 273).	Calomel. Saturated.	Calomel. 1·0*N*.	Calomel. 0·1*N*.	Quinhydrone. e_0.
15	0·03728	252·5	—	340·6	706·4
18	0·05773	250·6	286·4	338·0	704·4
20	0·05813	249·0	286·0	337·8	702·9
22	0·05853	247·5	—	—	701·2
25	0·05912	246·2	284·8	337·6	699·1
30	0·06011	243·7	283·6	337·2	695·4
38	0·06168	235·0	—	335·5	689·6
40	0·06207	234·0	—	—	688·1

(See pp. 35 and 47.)

TABLE 5.

Indicators and their Properties.

No.	Name.	Common name.	pH range.	Titration end-point K_{Ind}	Colour change.		Solvent.	Concentration per cent.	Volume of 0·05*N* NaOH per 100 mgrms.	Drops added to 10 c.c. of sample.
					Acid.	Alkaline.				
1	Thymol sulphone phthalein	Thymol blue	1·2– 2·8 8·0– 9·6	2·3 8·8	rose yellow	yellow blue	water	0·04	4·3	4
2	Tetra bromo phenol sulphone phthalein	Brom phenol blue	3·0– 4·6	4·1	yellow	purple	water	0·04	3·0	4
3	Dibromo *o*-cresol sulphone phthalein	Brom cresol purple	5·2– 6·8	6·1	yellow	purple	water	0·02	3·7	4
4	Dibromo thymol sulphone phthalein	Brom thymol blue	6·0– 7·6	6·9	yellow	blue	water	0·04	3·2	6
5	Phenol sulphone phthalein	Phenol red	6·8– 8·4	7·7	yellow	purple	water	0·02	5·7	4
6	*o*-Cresol sulphone phthalein	Cresol red	7·2– 8·8	8·2	yellow	purple	water	0·02	5·3	4
7	*m*-Cresol sulphone phthalein	Meta cresol purple	0·5– 2·5 7·6– 9·2	1·5 8·4	red yellow	yellow purple	95% alcohol	0·02	—	4
8	Tetrabromo *m*-cresol sulphone phthalein	Brom cresol green	3·2– 5·8	4·8	yellow	blue	water	0·02	—	4
9	Dichloro phenol sulphone phthalein	Chlor phenol red	5·0– 6·0	5·5	yellow	red	water	0·04	—	4
10	Dibromo phenol sulphone phthalein	Brom phenol red	5·4– 7·0	6·2	yellow	red	water	0·04	—	4
11	2·6.Dinitro-phenol	—	1·7– 4·4	—	colourless	yellow	water	0·10	—	—
12	2·4.Dinitro phenol	—	2·0– 4·7	—	colourless	yellow	water	0·10	—	—
13	2·5.Dinitro-phenol	—	4·0– 6·0	—	colourless	yellow	water	0·10	—	—
14	*p*-nitro phenol	—	5·0– 7·6	—	colourless	yellow	water	0·50	—	—
15	*m*-nitro phenol	—	6·5– 8·5	—	colourless	yellow orange	water	0·50	—	—
16	—	Alizarine yellow	10·0–12·0	—	pale yellow	orange	water	0·10	—	—
17	Tropaeolin-OO	Orange IV	1·3– 3·2	—	red	yellow	dilute alcohol	0·5	—	2
18	—	Methyl orange	3·1– 4·8	—	red	orange yellow	water	0·02	—	6
19	—	Methyl red	4·2– 6·3	5·1	red	yellow	60% alcohol	2·0	—	3
20	—	Neutral red	6·8– 8·0	—	red	yellow	water	1·0	—	3
21	—	Litmus	5·0– 8·0	—	red	blue	60% alcohol	2·0	—	15
22	Turmeric	Curcuma	7·8– 9·2	—	yellow	brown	dilute alcohol	1·0	—	4
23	Phenolphthalein	—	8·2–10·0	9·7	colourless	red	70% alcohol	1·0	—	10
24	Tropaeolin-O	—	11·0–13·0	—	yellow	orange	dilute alcohol	1·0	—	7

NOTES.—Nos. 1 to 6 are Clark and Lubs' (and Barnett's) indicators, Nos. 7 to 10 are Cohen's solutions, while Nos. 11 to 16 are the one-colour indicators of Michaelis and Gyemant. The remainder are useful indicators in general use, obtained chiefly from Kolthoff and Furman's work (see p. 87).

TABLE 6.

Indicator Errors and their Corrections.

No. (See Table 5.)	Temperature correction at 70° C.	Salt error corrections.		Protein error corrections.			
		0·5*M* NaCl.	1·0*M* NaCl.	1·0*M*.	3·0*M*.	10% gelatine.	5% peptone.
1 (acid)	0	−0·05	+0·05	−0·10	−0·12	+0·10	−0·20
1 (alkaline)	+0·4	−0·17	−0·22	−0·22	−0·34	+0·20	+0·05
2	0	−0·30	−0·35	−0·28	−0·43	+0·05	−0·30
3	0	−0·25	−0·26	−0·26	−0·31	+0·04	+0·10
4	—	−0·17	−0·26	−0·19	−0·29	+0·04	+0·07
5	+0·3	−0·15	−0·21	−0·21	−0·29	+0·20	+0·02
6	—	−0·17	−0·28	−0·28	−0·37	+0·20	+0·02
8	0	−0·20	−0·32	−0·26	−0·29	−0·10	−0·10
9	0·9	−0·18	−0·26	—	—	—	+0·05
10	—	−0·22	−0·26	—	—	—	+0·10
11	—	−0·30	—	—	—	—	—
12	—	−0·20	—	—	—	—	—
13	—	−0·13	—	—	—	—	—
14	+0·5	−0·05	—	—	—	—	—
15	—	−0·16	—	—	—	—	—
17	+0·45	+0·06	+0·23	—	—	—	−0·18
18	+0·3	+0·02	+0·23	−0·04	+0·12	—	−0·10
19	+0·2	+0·10	—	−0·05	−0·20	—	+0·13
20	+0·7	+0·10	—	—	—	—	—

See p. 97.

TABLE 7.

Permanent Inorganic Colour Standards for Clark and Lubs' Indicators.

Indicator.	pH range.	Red.	Yellow.	Blue.	Water.	Remarks.
Thymol blue (acid)	1·2 2·8	24·0 4·0	12·0 60·0	— —	64·0 36·0	Good
Brom phenol blue	2·8 4·2	— 17·5	50·0 —	— 82·5	50 —	Fairly good
Brom cresol green	3·6 5·2	1·3 6·5	33·0 —	— 93·5	65·7 —	Good
Methyl red	4·3 5·9	21·0 3·0	— 39·0	21·0 —	58·0* 58·0	Fairly good
Brom cresol purple	5·2 6·8	4·0 18·0	46·0 —	— 82·0	50·0 —	Poor

TABLE 7—*continued.*

Indicator.	pH range.	Red.	Yellow.	Blue.	Water.	Remarks.
Brom thymol blue	5·9 7·5	2·0 7·0	98·0 —	— 93·0	— —	Good
Phenol red	6·8 8·4	3·0 21·0	39·0 —	— 21·0	58·0 58·0*	Good
Cresol red	7·1 8·7	1·0 30·0	48·0 —	— 70·0	51·0 —	Good
Thymol blue (alk.)	8·1 9·7	1·2 13·0	50·0 —	5·0 87·0	43·8 —	Good

KEY.—*Red,* 20 per cent. cobalt nitrate. *Yellow,* 0·03 per cent. potassium dichromate. *Blue,* 10 per cent. cryst. copper sulphate. In all cases match against solutions containing 1 drop per c.c. of 0·02 per cent. indicator, except for thymol blue, where a 0·04 per cent. solution is used.

* Use 50 per cent. acetic acid in place of water. (See p. 89.)

TABLE 8.

PH Values Corresponding with Gillespie's Drop Ratios.

Indicator (numbers as in Table 5).

Drop ratio.	2	19	3	4	5	6	1 (Alkaline range).
1 : 9	3·1	4·05	5·3	6·15	6·75	7·15	7·85
1·5 : 8·5	3·3	4·25	5·5	6·35	6·95	7·35	8·05
2 : 8	3·5	4·40	5·7	6·50	7·10	7·50	8·20
3 : 7	3·7	4·60	5·9	6·70	7·30	7·70	8·40
4 : 6	3·9	4·80	6·1	6·90	7·50	7·90	8·60
5 : 5	4·1	5·00	6·3	7·10	7·70	8·10	8·80
6 : 4	4·3	5·20	6·5	7·30	7·90	8·30	9·00
7 : 3	4·5	5·40	6·7	7·50	8·10	8·50	9·20
8 : 2	4·7	5·60	6·9	7·70	8·30	8·70	9·40
8·5 : 1·5	4·9	5·75	7·0	7·85	8·45	8·85	9·55
9 : 1	5·0	5·95	7·2	8·05	8·65	9·05	9·75
Produce an acid colour with :—	1 c.c. 0·05*M* HCl.	One drop of 0·05*M* HCl.				One drop of 2 per cent. KH_2PO_4.	

See p. 93.

	0	1	2	3	4	5	6	7	8	9	1 2 3 4	5	6 7 8 9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4 9 13 17 4 8 12 16	21 20	25 30 34 38 24 28 32 37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4 8 12 15 4 7 11 15	19 19	23 27 31 35 22 26 30 33
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3 7 11 14 3 7 10 14	18 17	21 25 28 32 20 24 27 31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3 7 10 13 3 7 10 12	16 16	20 23 26 30 19 22 25 29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3 6 9 12 3 6 9 12	15 15	18 21 24 28 17 20 23 26
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3 6 9 11 3 5 8 11	14 14	17 20 23 26 16 19 22 25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3 5 8 11 3 5 8 10	14 13	16 19 22 24 15 18 21 23
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3 5 8 10 2 5 7 10	13 12	15 18 20 23 15 17 19 22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2 5 7 9 2 5 7 9	12 11	14 16 19 21 14 16 18 21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2 4 7 9 2 4 6 8	11 11	13 16 18 20 13 15 17 19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2 4 6 8	11	13 15 17 19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2 4 6 8	10	12 14 16 18
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·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

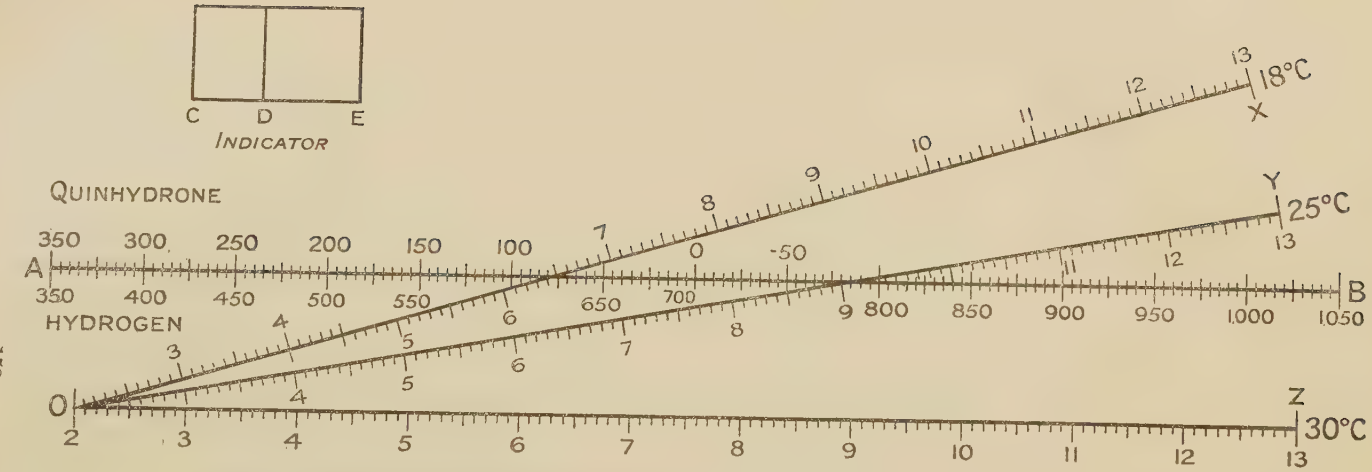

FIG. 24.—INSTRUCTIONS FOR USING THE HYDROGEN ION CONVERSION NOMOGRAM (see p. 72).

To Convert Millivolts into pH Values :—

Set the vertical line of the indicator corresponding with the particular calomel electrode in use (C for saturated, D for 1·0*M*, and E for 0·1*M* electrodes) at the reading in millivolts on the scale AB. (Use the upper scale for the quinhydrone electrode and the lower scale for the hydrogen electrode.) Then the vertical line marked C crosses the horizontal or oblique line (OX, OY, or OZ), representing the temperature of the experiment, at the corresponding pH value.

To Convert pH Values into Millivolts :—

Set the vertical line C of the indicator at the pH value on the line OX, OY, or OZ corresponding with the temperature used. Then the point at which the vertical line C, D, or E on the indicator, corresponding with the calomel electrode used, crosses the scale AB gives the E.M.F. in millivolts.

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